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SEPARATION AND CHARACTERIZATION OF SURFACTANTS PRESENT IN EMULSIONS PRODUCED IN ENHANCED OIL RECOVERY PROCESSES

FINAL REPORT

June 1988

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Final Report

By

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ABSTRACT

This study has been undertaken to characterize the surfactants that stabilize emulsions occurring in enhanced recovery operations of bitumen/heavy oil in Saskatchewan and Alberta. Knowledge about the nature of the stabilizing surfactants may help improve emulsion treating technologies and, ultimately, recovery operations. Both oil-in-water emulsions, found in steamflood operations, and tight (difficult-to-break) water-in-oil emulsions typical for fireflood-produced crudes were included in this investigation. The steamflood samples were collected from the Texaco Lone Rock and Canterra Meota projects and the fireflood samples from the Mobil Battrum, Murphy Eyehill and Mobil Fosterton N.W. projects.

Ultrafiltration using membrane permeation of the produced (free) water phases was the technique applied to separate the surfactants. Since the Eyehill and Fosterton emulsions were produced without free water, they were vigorously stirred with added water. After the unstable oil-in-water emulsions thus formed had broken, the separated free water phases were subjected to ultrafiltration. Determination of the total organic carbon content showed that the washing action had extracted substantial amounts of water-soluble organic materials.

Essentially zero permeation rates were obtained when using Polysulfone E500 (0.04 μm) membrane with fresh Meota oil-in-water emulsion, although good performance was achieved with a similar but aged (seven months) test emulsion. Various possible causes were identified and further investigated, including membrane type (other membranes evaluated were Cellulose Nitrate 0.01 μm, Nylon-66 0.1 μm and Nylon-66 0.2 μm) and supplier, membrane fouling, plugging of the membrane cell, sample oxidation, and operating temperature. The best permeation performance was achieved using Nylon-66 0.2 μm membranes, produced water feedstock with all free oil removed, and a permeation cell with the sintered membrane support plate cleaned before each run.

As a result of these investigations, it also appeared that the aging of emulsions might have been affected by a combination of exposure to air, mixing/circulation and long settling times. A subsequent aging study on a Lone Rock oil-in-water emulsion, which had been allowed to age in air-free drums for one day, one week and one month, respectively, confirmed that sample oxidation was a primary factor. This aging study revealed no differences between the three types of emulsion samples, either in permeation performance or in the infrared data of the subsequently isolated organic fractions.

Following chemical analysis of the raw permeates, three methods were used to isolate and/or concentrate the dissolved organic matter from the water phases: (1) water removal by freeze-drying or rota-evaporation; (2) extraction of the acidified permeates with ethyl acetate, followed by removal of the solvent; and (3) separation by column chromatography into acidic, neutral and basic fractions. The solid products from methods (1) and (2) were characterized by elemental analysis and infrared spectroscopy. The ethyl acetate extracts from method (2), the primary products isolated in this study, were further characterized by vapour pressure osmometry (for molecular weight determination), acid number determination, thermal gravimetric analysis, ^{13}C nuclear magnetic resonance (NMR) and gas chromatography/mass spectrometry (GC/MS). The chromatographic fractions were analyzed by infrared spectroscopy (IR) and GC/MS; they were too dilute for ^{13}C NMR spectroscopy. The identification of classes of species and individual species within the samples was mainly based on the ^{13}C NMR, GC/MS and IR analyses. Since equipment calibration with standard compounds fell outside the scope of this study, only approximate quantitative results were obtained.

Clear trends emerged with respect to the characteristics of the isolated materials. The major constituents in all five sample cases were aliphatic carboxylic acids, benzoic acid and derivatives, and phenol and derivatives. Differences were observed in the relative proportions of these constituents and these differences could be related to the origin of the material. Fireflood materials tended to be more aromatic, have a higher benzoic acids content, an average to low aliphatic carboxylic acids content, and contain only small amounts of phenols. The Battrum sample was characteristic for this class. Steamflood materials, on the other hand, tended to be more aliphatic, have a higher aliphatic carboxylic acids content, a moderate to low benzoic acids content, and contain high levels of phenols. The Lone Rock sample was a good representative of this type. The remaining three samples fell in between these two extremes. The Fosterton sample was closest to the Battrum material. The Eyehill and Meota samples formed the transition, with Eyehill having relatively high phenol levels and Meota having relatively high benzoic acid levels.

Because the isolated organic materials could not be redissolved in water, their surface active properties could only indirectly be measured using the original permeate solutions. Interfacial tension measurements on the raw permeates were inconclusive.

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1. INTRODUCTION

1.1 BACKGROUND

Increased exploitation of unconventional energy sources has manifested itself in recent years. Much attention is presently being focused on the mechanisms and economics of the recovery and use of heavy oil and bitumen. The sizable reserves of heavy oil and bitumen in Alberta and Saskatchewan cannot be extracted by conventional means to any significant degree due to their high viscosities. Improved recovery is, however, possible with enhanced recovery techniques such as steamflooding and in-situ combustion, both of which are presently in use in the field.

The oil recovered by using these methods is almost always produced in the form of oil-water emulsions. While in-situ combustion or fireflooding usually produces very stable water-in-oil (w/o) emulsions, both w/o emulsions and stable, reverse, oil-in-water (o/w) emulsions can be formed in steamflooding operations.

An emulsion, or a suspension of one liquid within a second immiscible liquid, is actually thermodynamically unstable. The stability and persistence of these emulsions are due to the presence of surfactants, which are partially soluble in both liquid phases. Surfactant molecules reside at the interfaces between liquid phases, with a polar portion of the molecule in the water phase and a nonpolar portion of the molecule in the oil phase. This orientation decreases the interfacial energy between particles of the two unlike phases and allows the existence of the two phases as an emulsion.

Some emulsions formed in oil recovery are broken into their oil and water phases merely by allowing them to settle or by the use of conventional practices such as applying heat. Firefloods, however, often result in extremely stable emulsions, which cannot be treated adequately by conventional treating methods. The development of more efficient treatment methods for this type of emulsions hinges in part on the progress we make with respect to developing an understanding of the characteristics of the surfactant molecules occurring in these emulsions, and of the role these surfactants play in stabilizing emulsions--one of the subjects of this study. The only technology currently available for treating fireflood emulsions is flash evaporation. Although capable of breaking these tight emulsions, it has the undesirable effect of concentrating salts in the oil phase, thus making upgrading and refining more difficult and expensive.

Drawbacks such as those inherent in flash evaporation are avoided in one recently reported method of breaking o/w emulsions: ultrafiltration.[1,2] This method involves passing the emulsion over a semipermeable membrane, which allows small molecules such as water to pass through its pores, while retaining the oil phase. Because the surfactant molecules are also able to pass through the larger membrane pores used in ultrafiltation, the decreasing surfactant concentration may result in the breaking of the emulsion. Membrane technology, when applied to treating oilfield emulsions, offers several potential advantages. Inorganic salts are expected to concentrate in the aqueous permeate, and hence the resulting desalted oil in the retentate would be better suited for upgrading and refining.

Another membrane permeation method, reverse osmosis, makes use of membranes with smaller pore sizes than those used for ultrafiltration. Because surfactants and salts are now concentrated in the retentate, the permeating water would be of sufficiently high purity to be used as boiler feed water. This recycling of water in steamflooding operations would be desirable in areas where water is scarce or where environmental restrictions prohibit the disposal of the produced water.

In this project, ultrafiltration will be used to separate the surfactants present in Alberta and Saskatchewan oilfield emulsions and to concentrate them in the aqueous permeate for easier subsequent analysis. Analyses will be carried out on all materials passing through the membrane. These analyses will serve not only to characterize any surfacants present in the permeated aqueous phase, but also to indicate the potential of ultrafiltration as a desalting technique.

1.2 OBJECTIVES AND SCOPE

1.2.1 Study Objectives

- The objectives of this research project were to isolate and characterize the surfactants that stabilize emulsions occurring in enhanced recovery operations of bitumen/heavy oil in Saskatchewan and Alberta.

- Ultrafiltration technology was to be used to achieve the separation of the surfactants from the emulsions and all permeated material was to be characterized.

- As a modification of the original objectives outlined in the Request for Proposal (RFP), equal emphasis was to be placed on oil-in-water emulsions (from steamflood operations) and water-in-oil emulsions (from fireflood operations), provided a method could be developed for the ultrafiltration of the latter type of emulsions.

1.2.2 Scope of Work

As a consequence of the exploratory nature of this research project, a number of experimental problems were encountered and unexpected results recorded. In order to overcome these problems and accommodate new insights as they developed, various changes were made to the original Work Statement as outlined in the RFP. These changes amounted to a considerable expansion of the original Scope of Work.

The following defines the revised Scope of Work and summarizes the work completed.

A. Literature Review

The existing information regarding the nature of surfactants identified in petroleum reservoirs and their role in emulsion stabilization and oil recovery were reviewed. Membrane separation techniques, as applied to heavy oil/bitumen emulsions, were also included in the survey. The reviewed material was categorized into the following topics:

- The chemical and physical characteristics of naturally occurring surfactants in petroleum reservoirs.
- Formation of surfactants during thermally enhanced recovery of bitumen and heavy oil.
- The role of surfactants in the stabilization of bitumen/heavy oil emulsions produced during thermal recovery.
- The role of surfactants in the recovery of bitumen and heavy oil.
- The use of ultrafiltration and reverse osmosis for water/bitumen/heavy oil systems and for the selective removal of surfactants from other oil/water systems.

B. Sample Acquisition and Ultrafiltration

Two steamflood (o/w emulsion) samples and three fireflood (w/o emulsion) samples were collected and permeated. The fireflood samples underwent a pretreatment step (water wash) to render them amenable to permeation. Various membranes were evaluated before one was identified that performed satisfactorily with fresh emulsion samples. An aging study was conducted to determine the effect of aging on the nature of emulsions.

C. Surfactant Isolation and Characterization

Three methods were used to isolate the dissolved organic materials concentrated in the raw permeates.

- Water removal by freeze-drying or rota-evaporation.
- Acidification, followed by extraction with ethyl acetate and subsequent removal of solvent. (The original acid precipitation step was skipped, since it only produced precipitates with the steamflood samples, and then only in very small quantities.)
- Column chromatographic separation into acidic, neutral and basic organic fractions. (The procedure originally proposed only separated the aqueous permeates into organic and inorganic fractions.)

The raw permeates as well as the products isolated according to the above three methods were analyzed following a modified Schedule of Determinations (see Table 2). Primary analysis methods for the characterization of the two most important surfactant-containing products (i.e. the ethyl acetate extracts and the chromatographic fractions) were infrared spectroscopy (IR), ^{13}C nuclear magnetic resonance (^{13}C NMR), and gas chromatography/mass spectrometry (GC/MS). A detailed interpretation of all characterization results concludes the study.

1.3 LITERATURE REVIEW

1.3.1 Summary

A review of the literature was performed on surfactants in heavy oil/bitumen emulsions. Emphasis was placed on the characterization and properties of naturally occurring surfactants in petroleum reservoirs. Surfactants not originally present but formed during thermally enhanced recovery were also of interest. The role of these surfactants in both the stabilization of emulsions and in the recovery of heavy oil and bitumen was reviewed. Another area of interest was the application of ultrafiltration and reverse osmosis to the separation of water/heavy oil systems and to the selective removal of surfactants from oil/water systems. Results from eighty publications are summarized and compared. Discrepancies between different authors are discussed and possible causes for these disparities suggested.

1.3.2 The Chemical and Physical Characteristics of Naturally Occurring Surfactants in Petroleum Reservoirs

This survey will review the literature published on the nature of surfactants in petroleum reservoirs. Studies of surfactants in petroleum reservoirs where oil is recovered by primary methods will reveal the nature of surfactants naturally present in reservoirs, while studies on oil obtained from secondary thermal recovery schemes will indicate the type of surfactants produced during thermal recovery. Experimental work on surfactants produced by alkali addition will also be included. The precursors of these surfactants are thought to include acids activated at high pH with the anions exhibiting surface active properties. The naturally occurring surfactants present in the oil-water system are therefore partitioned between active and inactive forms, both of which are of interest. It should be mentioned that very little has been published on surfactants present in oil-water systems at low or neutral pH.

There have been many studies performed on the identification of naturally occurring surfactants in oil-water systems and yet, because of the multitude and complexity of compounds involved and the paucity of work done in certain areas, it must be concluded that these surfactants are not well characterized.

Studies in which many organic compounds were isolated and characterized have been performed on heavy oil/bitumen, produced water and emulsions. Some of the characterized compounds exhibited similarities to compounds shown by other authors to be surface active. If no evidence of surface activity was reported, however, these papers will not be discussed in this survey.

Unfortunately, there have been very few studies performed on surfactants found in oil-in-water emulsions. Obviously, this is a fertile area for study. Types of studies on naturally occurring surfactants comprised the following:

i) Materials from the oil-water interface were isolated, and because of their presence at the interface were presumed to be surface active.

ii) The oil-water system was separated into fractions based on factors such as solubility, distillation temperature, etc. These fractions were then recombined with one fraction eliminated and emulsification attempted to determine which class was responsible for emulsion formation.

iii) The oil-water system was separated into fractions as outlined above. Each fraction underwent measurements such as interfacial tension (IFT) or surface tension measurements to determine surface activity. (Low interfacial tensions, for example, are required for emulsion formation and are a direct measurement of the number of surfactant molecules replacing solvent molecules at the interface.)

One problem common to all three of these methods involved the presence of more than one compound or type of compound in the isolated fraction. As an example, consider the following: a class of compounds is isolated and found to have surface active properties. Infrared spectroscopy indicates that acids are present. In this case, it may not be the acids causing surface activity, but their presence overwhelms the spectroscopic detection of the compound in that fraction exhibiting surface active properties.

Measurements of surface tension or interfacial tension of oil-water systems also have inherent problems when applied to determining surfactant effectiveness. The lowering of surface tension at the air-water interface is not convincing evidence of being surface active at the oil-water interface. Measurements of the interfacial tension between oil and water are controversial evidence of surfactant ability. Dodd,[1,3] and Gaulier and Pacsirszky[4] have indicated that the presence of interfacial films invalidates the measurement of interfacial tension by the pendant drop and other classical methods. Capelle[5] also indicated some of the limitations involved in extrapolating interfacial tension measurements using the spinning drop technique to determine surfactant effectiveness.

Many different compounds and different types of compounds have been identified as naturally occurring surfactants. Surfactants produced in alkali solution will be discussed as if they were naturally occurring surfactants. With the exception of the early work of Dunning et al[6] and Dodd et al,[7] all studies on surfactants present in crude oil considered surfactants active in crude oil-alkali. Alkaline solutions were also considered for almost all studies identifying oil sands surfactants.

As referenced below, oil sands surfactants were universally identified as being acidic in nature, while crude oil surfactants were identified as being carboxylic acids, phenols, porphyrin and metal complexes and members of various solubility and distillation classes.

Carboxylic acids and their anions have been widely reported as being responsible for interfacial activity;[3,8-18] however, much of this evidence is by implication.[3,11,14,16,17] Seifert and Howells[8] presented strong evidence when they showed that a fraction from a California crude containing carboxylic acids (as indicated by IR spectroscopy) evinced interfacial tension lowering. Seifert continued in later papers to show that carboxylic acid content correlated with the degree of interfacial activity[19] and more fully elucidated the structures of the carboxylic acids (using gas chromatography, mass spectroscopy, fluorescence and ultra-violet (UV) spectroscopy), identifying mainly polycyclic naphthenic, mono- and diaromatic carboxylic acids.[19,20] Not all of the compounds in the interfacially active fraction were identified. The identified polycyclic naphthenic, mono- and diaromatic carboxylic acids were actually the least polar molecules of the active fraction, and hence other, as yet unidentified molecules, could be the material responsible for surface activity.

Negative aspects of the Seifert study included the measurement of interfacial tension after only five seconds when other authors[21] insist that a 15-minute equilibrating period is required for valid interfacial tension measurements. Seifert et al[8] also admitted that the interfacial activity of their surface active fraction was increased as a result of the workup procedure.

Ali[12] used foam fractionation to isolate materials present at the oil-water interface from Athabasca oil sand and identified carboxylic acids using IR, UV and NMR spectroscopy. Sulfonic acids were also identified as being present in the interface materials.[12]

Naphthenic acids,[1,2,3,19,20] humic acids,[11,22-24] and fulvic acids[22,25] have been shown to be present in bitumens/crude oils, but no evidence, with the exception of Seifert's work,[19,20] was found relating these compounds to interfacial activity. Nader et al[1] and Zenon[2] reported the removal of naphthenic acids with the permeating water fraction during ultrafiltration of oil-in-water emulsions. Because the removal of these compounds was followed by breaking of the emulsion, they concluded that naphthenic acids supported emulsion stability. Humic and fulvic materials have only been associated with oil sands; no reference was found alluding to their presence in crude oils.

Neumann[26] presented evidence that phenols were responsible for surface activity in West Germany crude oil. However, this was refuted by Seifert and Howells[8] for the case of California crude oil. They isolated phenolic material from carboxylic material in an interfacially active fraction containing both types of compounds and showed that the isolated phenol fraction was interfacially inactive. In a later paper, Seifert[27] concluded that phenols have a negative synergistic effect on the interfacial activity of carboxylic acids in a crude oil fraction containing both types of compounds.

Kessick[28] published a paper dealing with surfactants of reverse emulsions from Lloydminster crude oil, relating phenolate anions to oil-in-water emulsification. He reasoned that phenols ionize sufficiently only at high pH (pH 11-12) and that phenolate anions easily react with oxygen. Thus if phenols did act as surfactants, there would be a sufficient number to produce an emulsion only under deaerated, high pH conditions. This was confirmed by experiment.

Porphyrins, metalloporphyrins and other metal organometallic complexes have been found in interfacial material isolated from California, Oklahoma and Venezuela crudes.[6,7] These complexes were shown to be present in fractions which lowered the interfacial tension (as measured by the pendant drop method) and contributed to interfacial film formation. This was refuted by Jang et al,[10] who concluded no interfacial tension lowering resulted from the presence of porphyrins.

It is possible that other compounds in the isolated fractions were responsible for the interfacial tension lowering, but the strong effect of metal complexes on film formation was confirmed by Donaldson and Crocker.[29] They reported that crude oils without spontaneous interfacial film formation did so with the addition of small amounts of Ni, V or Cr water-soluble salts.

The asphaltene fraction (n-pentane insoluble fraction) from various crude oil systems was shown to exhibit interfacial tension lowering properties[7,19,30] and has been proposed as being an interfacial film forming material by several authors.[14,31-33] Greenlee,[32] Van der Waarden[33] and Strassner[34] added asphaltene from crude oil to organic/aqueous systems and found that emulsion stability increased for increased asphaltene content. Khulbe *et al*[30] concluded that since the deasphalted Lloydminster crude oil had the same interfacial activity level as the original untreated oil, asphaltenes alone were not responsible for surface activity. Pasquarelli and Wasan[31] showed that asphaltenes did exhibit interfacial tension lowering, but claimed resins played the major role in interfacial activity and film formation. The complexity of the role of asphaltenes in interfacial activity was noted and attributed to peptization and precipitation of asphaltenes.

On the other hand, Runnels and Engel[21] claimed that the asphaltene fraction of an Arkansas crude was void of surface activity. This apparent contradiction can be resolved when one examines the concentrations of the asphaltene fraction used in each study. The Runnels and Engel study[21] used a 2% asphaltene-in-benzene sample and their results are similar to those of a sample of 2.1% asphaltene-in-toluene sample used by Khulbe *et al*.[30] Khulbe *et al* based their conclusions that asphaltenes were responsible for interfacial activity in crude oil-alkali systems on the interfacial tension lowering of a second 22.3% asphaltene-in-toluene sample.

In one of the few studies on oil-in-water emulsions, Cottingham *et al*[35] showed that pentane insoluble portions (asphaltenes) of distilled crude and filtered crude oil from retorted western U.S. shale oil possessed emulsifying ability.

Resins have been indicted as being responsible for IFT lowering by Layrisse et al[9] and Pasquarelli and Wasan.[31] Khulbe et al[30] published contradictory results, showing that the resinous fraction exhibited low but not ultralow IFT, which increased with time. Resins have also been mentioned along with asphaltenes as being film forming compounds.[31,32,34] Pasquarelli and Wasan added asphaltenes and resins to crude oil/aqueous systems and found that the resulting IFT was decreased. They theorized that precipitation of asphaltenes released the resins from peptization and allowed them to adsorb at the interface, forming an interfacial film which lowered IFT.

Kimbler et al[36] discovered that interfacial films in systems composed of fractions of a New Mexico crude oil and water formed with the resin fraction, but not for the asphaltene fraction. Their studies on a Texas crude, however, gave the opposite result; film formation occurred for the water/asphaltene fraction and not for the water/resin fraction. Obviously, the nature of the crude has a great influence on film formation and on the effectiveness of any given surfactant.

Aromatic compounds have been found to have no interfacial activity for a Venezuela crude[9] and very little interfacial activity for an Arkansas crude.[21] In apparent contradiction, mono- and di-aromatics were found to have considerable interfacial activity for a Lloydminster crude.[30] Researchers have reported no interfacial activity for the saturate fractions of crude oils.[9,21,30]

Workers, who have separated crude oil into fractions based on polarity, almost invariably reported the most polar fractions as being the most interfacially active.[10,21,29] Khulbe et al[30] presented results which showed that the polar (resinous) group exhibited low but not ultralow IFT.

A few authors have separated crude oils into distillation fractions and found that the highest boiling cuts exhibited the greatest degree of interfacial activity.[31,37,38] Hasiba and Jessen[38] collected a fraction of Texas crude oil which distilled at 371°C. Since this fraction exhibited surface activity, the film formed at the oil/water interface was isolated by inserting a glass slide into the interface. The material, analyzed by IR and mass spectroscopy, was found to contain polar compounds such as aliphatic esters of aromatic acids. Because of the high distillation temperatures involved, the identified compounds may not reflect the true nature of the polar compounds due to the loss of lower distilling materials and possible reactions occurring during the high temperature distillation.

Obviously, many different compounds and compound types have been concluded to be naturally occurring surface active agents. Differences in conclusions could arise from a number of reasons. Different oil samples have widely varying chemical properties and the nature of surfactants present in the oil depend on the type of oil. A classic example of this is reported by Kimbler *et al.*[36] For a New Mexico crude oil, the resin fraction formed interfacial films when contacted with an aqueous layer while the asphaltene fraction formed no interfacial film. The opposite result occurred with the resin and asphaltene fractions of a Texas crude.

Studies relying on interfacial tension measurements to identify surface active chemicals often measure IFT using different parameters. IFT measurement is dependent on pH, solvent and the length of time before measurements are taken--parameters that vary widely from one study to another.

Another cause of apparent opposing conclusions from different authors involves the different schemes and procedures used to divide crude oils into fractions based on solubility or distillation properties. Because of this, one solubility class from one set of researchers may overlap with other classes used by other workers. Acidic compounds are expected to reside mainly in the resinous fraction of crude oils. Components in the resin fraction should also be present in the most polar fraction.

Thus with the exception of Khulbe *et al*, who concluded that asphaltenes and mono- and di-aromatics were responsible for the interfacial tension lowering of Lloydminster crude against caustic solution, interfacial activity in crude oils is attributed to compounds in the fraction described as being acidic, resinous or highly polar, and the asphaltene fraction. As mentioned previously, naturally occurring surfactants in bitumen have been universally identified as being acidic in nature.

Some papers have suggested that more than one type of component is responsible for IFT lowering.[30,39] Sharma *et al*[39] presented a theoretical model, which qualitatively explains IFT behaviour if it is assumed that two species are responsible for IFT lowering. They claimed that, theoretically, one component should be a low molecular weight acid and the other component a higher molecular weight compound.

1.3.3 Formation of Surfactants During Thermally Enhanced Recovery of Bitumen and Heavy Oil

This topic is very sparsely studied if one discounts the simple addition of alkali to activate surfactants in bitumen/heavy oil recovery. The latter was covered in Section 1.3.2.

In the case of in-situ combustion, because of the temperature variation from the front (400-700°C) to lower temperature zones, two types of reactions are expected to occur.[40] Combustion or total oxidation is expected to occur in high-temperature zones (temperatures higher than 316°C), while partial oxidation is anticipated in low-temperature zones (temperatures lower than 316°C). Low-temperature oxidation of oil is expected to yield oxygenated compounds, including carboxylic acids, aldehydes, ketones, ethers, alcohols and hydroperoxides.[40-42]

These reactions have been simulated in laboratory studies of bitumen oxidation.[41,43] Moschopedis and Speight[42] oxidized bitumen and bitumen fractions using the addition of oxygen under mild conditions and catalyzed by metal salts. They found that general trends in the oxidation of bitumen involved the formation of more complex materials of higher molecular weight and incorporation of oxygen. The following oxidation scheme was proposed:

$$\text{Oils} \xrightarrow[M^{n+}]{O_2} \text{resins} \xrightarrow[M^{n+}]{O_2} \text{asphaltenes}$$

Thus, resins and asphaltenes, both of which have been previously implicated as having surface active properties, are produced by oxidation. They also found that oxidation decreased the solubility of asphaltenes. This could have the effect of releasing resins from peptization when asphaltenes are precipitated, as suggested in the theory of Pasquarelli and Wasan.[31] The released resins would then act as surfactants, thus explaining why surface activity also increased with oxidation.

The findings of Redford and Cotsworth[43] are in contrast: ozonolysis of bitumen was again limited to the resin and asphaltene fractions, but resulted in lower molecular weight and lower sulfur content. They concluded that the compounds synthesized by oxonolysis were surfactants. The increased solubility in water and the highly oxygenated character of the products, which they assumed were acidic, were the reasons on which they based this assumption.

Perhaps one reason behind this experimental discrepancy involves the use of metal salts in the work of Moschopedis and Speight.[42] They admitted that the presence of metal salts not only affected the rate of oxidation but also the nature of the products.

1.3.4 The Role of Surfactants in the Stabilization of Bitumen/Heavy Oil Emulsions Produced During Thermal Recovery

Surfactants play a vital role in the stabilization of oil-water emulsions: without the presence of a surfactant or some other stabilizing agent, two liquid phases cannot form an emulsion. This is due to the thermodynamic instability of an emulsion relative to the two bulk liquids. The term "emulsion stability" is, therefore, taken to mean resistance to coalescence of the dispersed droplets.

Emulsion stability is at an optimum at a particular concentration of surfactant, and that concentration is determined by a number of mechanisms involved in surfactant stabilization of emulsions.

The mechanism most often measured and correlated with emulsion formation and stability is the lowering of the interfacial tension between the oil and water phases. When surfactants replace solvent molecules at the oil-water interface, the interfacial tension (interfacial free energy per unit area of interface) decreases. This decrease in IFT is due to the orientation of the surfactant molecule with its hydrophilic end towards the water phase and its hydrophobic end towards the oil phase. This orientation results in stronger interactions between the similar chemical groups rather than the weak interactions between the dissimilar oil and water molecules. A decrease in the free energy and hence interfacial tension (IFT) results. As a result of lower IFT a larger surface area of interface between the oil and water phases can be maintained; formation of emulsions are now possible.[44]

While the lowering of IFT is instrumental in enabling the emulsion to form, it is also accepted as a mechanism in emulsion stabilization by surface active molecules. Perhaps too much emphasis is placed on this factor when characterizing surfactants. For example, when chemicals are tested for use in surfactant flooding, workers often use ultralow IFT as the sole criterion for selection of a commercial surfactant. Vinatieri[45] showed that the systems (Oklahoma crude-water-commercial surfactant systems) with the lowest IFT's did not support the most stable emulsions. One region of a phase diagram of an oil-water system showed rapid coalescence and high IFT while another region of rapid coalescence had low IFT.

Wasan et al[46] concluded that IFT did not correlate with the coalescence time of single drops of Illinois or Oregon crude in oil-in-water (or reverse) emulsions. Drop stability was expected to relate directly to emulsion stability.

Interfacial tension lowering is also involved in other aspects of the role surfactants play in emulsion stabilization. For example, the formation of a third phase or interfacial film by surface active materials is thought to result in a decreased IFT.[47,48]

Puig et al[47] and Isaacs et al[48] believe that the surfactant role is to form a third phase of undetermined nature (liquid crystals, microemulsion, membrane of solid particles have all been suggested), which yields ultralow apparent interfacial tensions between the water and oil phases. The apparent IFT is then actually the sum of the IFT between this phase and water and the IFT between the third phase and oil. Film formation also stabilizes emulsions by acting as a physical barrier to coalescence so that rupture of the film is necessary for coalescence.[14]

A paper was recently published on the formation of thin, solid films or membranes constituting a third phase at the interface.[16] This paper casts doubt as to whether such films were present during fluid flow in the reservoir. Apparently, films at the bitumen/water interface are not formed in the absence of light but are photolytically induced. Hence, film formation as a mode of emulsion stabilization by surfactants could be discounted under reservoir conditions.

Several papers have been published regarding the nature of the surfactants responsible for film formation in both bitumen/water and crude oil/water systems. This has been discussed in Section 1.3.2 on the chemical nature of surfactants. Classes of compounds implicated in film formation include asphaltenes,[14,31-33] resins,[31,32] polar materials[38] and organic metal complexes.[6,7,29] Both Greenlee[32] and Van der Waarden[33] found that film formation, and hence emulsion stability of water-in-oil emulsions, peaked when asphaltenes released the resins from peptization and allowed them to diffuse to the interface. There the resins would form an interfacial film, which lowered the IFT and increased the interfacial charge.

Interfacial viscosity is another parameter of emulsion stability and is related to formation of interfacial films. Very rigid films, made up of high molecular weight surfactants, have high interfacial viscosities and impede coalescence of emulsions. Vinatieri[45] attributed the slow coalescence rate of high-viscosity interfaces to a decrease in the mass transport across the interface, which is necessary for attaining equilibrium. Wasan et al[46] showed interfacial shear viscosity correlated with coalescence time of single drops in crude Illinois or Oregon oil-in-water emulsion. Wasan and Mohan,[47] however, found that the effect of the addition of commercial surfactant to Middle East crude oil-brine systems was to decrease interfacial viscosity. This is not a result of the effect of the commercial surfactant on an oil-brine system itself, but rather the relative effect of the commercial surfactant compared to the natural surfactants present. The commercial surfactant molecules replace natural surfactant molecules rather than solvent molecules at the interface. The interfacial viscosity is therefore decreased relative to the natural surfactant system rather than relative to a system with no surfactant present.

Wettability properties of the surfactants also play a role in stabilizing emulsions. Van der Waarden[33] theorized that surfactants can most easily form a film of solid particles and hence produce a more stable emulsion when the surfactant particles are wetted by both oil and water phases. Usually, however, wettability is more important in determining whether the emulsion inverts rather than whether it will coalesce. Surfactants present at the interface preferentially wet either the oil phase or the aqueous phase. The preferentially wet phase, which will also be the phase in which the surfactant is more soluble, then forms the continuous phase of the emulsion and hence determines whether an oil-in-water or water-in-oil emulsion is formed.[44]

Almost all of the previous discussion of the modes by which surfactants stabilize emulsions has pertained to water-in-oil emulsions. The presence of a charged layer at the interface, however, is considered very significant for the stability of oil-in-water emulsions. Greenlee[32] states that electrically charged films stabilize oil-in-water emulsions, while water-in-oil emulsions are better stabilized by uncharged and viscous or rigid films. Wasan _et_ _al_[46] and Levine and Sanford[50] correlated a large measurement of interfacial charge with high stability of oil-in-water emulsions. Takamara _et_ _al_[51,52] also indicated the importance of interfacial charge relative to emulsion stability for bitumens. Reddy and Fogler[53] showed that acoustically formed oil-in-water emulsions with no surfactants present were stabilized by electrostatic charges. For non-acoustically formed oil-in-water emulsions, surfactants play the analogous role of forming a negative charge at the interface, probably by loss of protons from carboxylic acids.

Pasquarelli and Wasan[31] found a correlation of maximum interfacial charge with minimum IFT and hence emulsion stability for water-in-oil emulsions of California crude/alkali systems.

Electrophoretic mobility is expected to play a role in the formation rather than the maintenance of emulsions. For emulsion formation, a high electrophoretic mobility is desired so that surfactants reach the interface quickly to lower IFT and promote emulsion formation.

Differences in the factors affecting the stability of oil sands emulsions compared to crude oil emulsions often involve the ubiquitous presence of clays, quartz and other fine particles in oil sands emulsions. These fines can promote emulsion formation and stability through film formation and wettability changes, but are not necessarily considered surfactants. However, naturally occurring surfactants interact with these fines and can be partially adsorbed.[84,85]

1.3.5 The Role of Surfactants in the Recovery of Bitumen and Heavy Oil

Emulsification as it relates to oil recovery is more complex than immediately apparent: stable emulsions increase 'oil recovery' in the transportation of the oil from the reservoir to the surface. However, if the emulsion is too stable, the efficiency of the 'oil recovery' from the emulsion is decreased. The use of the term 'oil recovery' in two different contexts explains why some authors equate emulsion stability with good oil recovery and others with poor oil recovery. Hence, the discussion of the role of surfactants in oil recovery will be divided into two topics: (1) the role of surfactants in the transport of the crude oil/oil sand from the reservoir to the surface, and (2) the role of natural surfactants in the separation of oil from emulsion. The latter topic is usually fairly straightforward, with the exception of the hot water process applied to the separation of bitumen from Alberta oil sands. In this case, the role of surfactants is important and complex. This will be discussed in more detail.

In the in-situ combustion recovery method, a combustion front is produced by burning part of the reservoir oil by oxygen or air injection. The high burn temperatures substantially decrease the oil viscosity and permit mobilization of the oil. The role played by surfactants in this recovery scheme is the modification of viscosity caused by emulsification. Often, viscous water-in-oil emulsions are produced, a phenomenon that does not assist in oil recovery. When very tight water-in-oil emulsions are produced, heat, time, and occasionally more rigorous treatment such as flash evaporation are necessary for treatment.

In some crude oil reservoirs, oil-in-water emulsions can be produced by the in-situ combustion recovery method.[56] These emulsions have viscosities close to that of water and the favorable flow characteristics associated with low-viscosity fluids. Oil-in-water emulsification is thought to occur in front of the combustion zone with emanating hot gases and steam providing the mixing energy necessary for emulsification. The aqueous transporting phase arises from formation water and condensing steam.[56]

Oil-in-water emulsification would be enhanced by the use of wet combustion as a recovery method. Surfactants slightly more soluble in the aqueous phase than the oil phase favor reverse emulsion stabilization.[44] The presence of naturally occurring surfactants with this characteristic in the petroleum reservoir would then increase oil recovery.

Oil recovery by steamflooding also relies on thermal energy to decrease the viscosity and improve the flow of the oil. Production of an oil-in-water emulsion is favored by steamflooding and especially by cyclic steam recovery operations. This is due to the high injection rate of steam which provides excellent mixing and enables emulsification.

The formation of an oil-in-water emulsion is thought to contribute to both recovery rate and ultimate recovery.[56] An increase in recovery rate is anticipated because of the presence of the oil in the mobile emulsion phase. Oil previously considered irrecoverable because of impermeability becomes mobile upon emulsification and the amount of recovered oil is increased.

Other factors affected by surfactants in recovery by steam injection include permeability of the reservoir, interfacial tension and wettability properties of the reservoir.

Permeability variations in the reservoir cause residual oil to be left behind in the reservoir after steamflooding. When the rock matrix is too permeable, water flows too easily through some parts of the reservoir and, since the path of least resistance is followed thereafter, the volume reached by steam is kept small. Emulsification prevents the domination of these 'thief zones' by increasing the viscosity of the displacing water and enlarging the steam zones.[48,57] Permeability also plays a role when the permeability of the rock matrix is too low to permit the displacing water or steam to reach oil trapped in the rock pores. Pasquarelli et al[58] showed that by adding more resins asphaltenes would be prevented from precipitating and plugging pores in the rock. The resultant increase in permeability would enhance oil recovery.

Low interfacial tensions between the reservoir oil and the added aqueous phase are necessary to overcome the capillary pressures preventing the oil from leaving the pore space.[47] Isolated blobs of trapped oil can be forced through narrow openings to join the continuous oil if the interfacial tension is sufficiently low, a phenomenon made possible by surfactant action.[37,59,60]

Donaldson and Crocker[29] claimed that wettability was the most important factor affecting residual oil and fluid flow. Surfactant effects on wettability can be explained by simple models accounting for ionic attraction and repulsion. Assuming that an acidic natural surfactant is present, at high pH the predominance of the acid anion will negatively charge the crude oil surface. The surface of the crude will then repel the negatively charged silica surface and support the formation of a water film separating the oil and rock matrix. At low pH the crude oil surface will be positively charged and experience attraction to the rock surface, causing it to be oil wet.[69] Oil wettability of the rock matrix will cause water to be displaced from pores while oil is retained, thus decreasing waterflood recovery.[29]

In the hot water process for recovering bitumen from Alberta oil sands, oil sand and alkali are slurried together, screened to remove inorganic particles and aerated to enable easy collection of the bitumen as froth. Schramm et al[18,61,62] published a series of papers dealing with the role of natural surfactants in the hot water-alkali process of bitumen recovery from Athabasca oil sands. They discovered that the efficiency of the hot water flotation process attained a maximum at a particular concentration of free surfactant. (They measured the concentration of carboxylate anions in interfacial material isolated by foam fractionation.)

This free surfactant concentration corresponded to a maximum of electrophoretic mobility and interfacial charge of bitumen globules. As surfactants are activated by alkali addition, the acid anions adsorb at the bitumen interface, resulting in high electrophoretic mobility and interfacial charge. This enhances the repulsion of the negatively charged bitumen droplets and solids, and increases the separation of the bitumen and sand. Schramm et al[18] also theorized that not only do the surfactants promote bitumen aeration but they also boost solids, contributing both positively and negatively to the efficiency of the hot water flotation process. Baptista and Bowman[63] confirmed this by isolating interfacial material by foam fractionation and demonstrated that this material contributed to solid flotation. The material was identified using IR spectroscopy as being composed of naphthenic acid salts and carboxylic acid salts.[63] Confirmation of the importance of electrical charges to bitumen recovery by the hot water process is provided by Takamara.[62]

1.3.6 The Use of Ultrafiltration and Reverse Osmosis for Water/Bitumen/Heavy Oil Systems and for the Selective Removal of Surfactants from other Oil/Water Systems

The use of ultrafiltration for the purpose of emulsion breaking has been examined for oil-in-water emulsions. With the exception of a series of papers by CANMET researchers[1,64-67] and a report prepared for CANMET by Zenon,[2] the oil-in-water emulsions examined by most other workers usually comprise various lubricating oils and other oils much lighter than the bitumen/heavy oil systems of interest.[68-73] Stephens *et al*[70] published results on ultrafiltration of oil-in-water emulsions containing Venezuela crude, as well as other samples of oil-in-water emulsions of lubricating oil, fuel oil and kerosene. Dubey[74] also published work on the ultrafiltration of crude oil (27°API) with commercial sulfonate surfactants and polymers. It appears that no work has been published on the ultrafiltration of water-in-oil emulsions. Problems anticipated for the ultrafiltration of such emulsions comprise a prohibitive amount of membrane fouling by oil, and low concentrations of isolated surfactants due to their likely preferential solubility in oil. Kutowy *el al*[75] used polysulfone membranes to clean both light and heavy oils of inorganic matter and heavier oil components such as asphaltenes. Although flux rates were very low (less than 7.1 kg/m^2/day for light oils), ultrafiltration was made possible by diluting heavy oils with naphtha and preparing the membranes for a non-aqueous environment using a solvent exchange procedure.

Emulsion breaking is thought to occur on the membrane surface when a sufficient amount of surfactant permeates through the membrane and insufficient surfactant remains to support an emulsion.[1,2,66,67] This theory was not proven in practice by Stephens *et al*,[70] who found tight oil-in-water emulsions did not spontaneously break during ultrafiltration. They attributed this to the high solubility of the surfactants in the oil phase, a theory which they contradicted later in their report when they demonstrated the preferential solubility of the surfactants in the water phase.

Another method of emulsion breaking attempted by Stephens et al[70] involved the use of reverse osmosis to dewater the emulsion and increase the saline concentration of the retentate. Upon addition of calcium chloride, the retentate inverted to a water-in-oil emulsion, which was then treated using settling methods. This process was not economically viable.

Problems were reported with membrane fouling for thin film composite, cellulose acetate and polyvinyl chloride acrylonitrile copolymer membranes.[68,71,74] These problems were abated by stirring the input emulsion, frequent membrane cleaning, coarse prefiltration and presettling of the emulsion, and the addition of an emulsion stabilizer. Beaton and Hasleden found that the addition of 5-15% by weight of a commercial surfactant improved flux rates which had decreased by oil fouling of the membrane.[68] This finding was confirmed by Goldsmith et al,[69] who attributed the lack of membrane fouling to the presence of detergent emulsifiers in the coolant oils studied. Zenon[2] found several membranes which were more resistant to oil fouling.

Permeation of surfactants with the water phase from oil-in-water emulsions has been demonstrated by the CANMET group.[1,2,65-67] A polar compound was isolated from the water permeate, and IR analysis yielded a spectrum similar to that of naphthenic acids.[1,2,67] Subsequent breaking of the emulsion after removal of the polar material lent impetus to the theory that this polar material was surface active.

Separation of a commercial sulfonate surfactant from a Nujol oil-in-water emulsion has been effected by Baddour.[73] To increase the amount of recovered surfactant in the water relative to the oil phase, he added a co-surfactant such as 2-octanol. Dubey[74] reported the permeation of a water-soluble commercial sulfonate surfactant with cellulose acetate membranes and permeation of both water- and oil-soluble sulfonates with Abcor HFM-251 polymeric membranes.

Stephens et al[70] used ultrafiltration with a tight membrane to retain and concentrate the surfactant in the retentate of a surfactant-brine solution. They used a high concentration of a commercial petroleum sulfonate surfactant and thought that, since the concentration of the surfactant was above the critical micelle concentration, micelles formed and could not pass through the membrane. The retentate then underwent settling, with the surfactant micelles preferentially staying in the water phase. Reverse osmosis of the separated water phase was used to further concentrate the surfactants.

Reverse osmosis of the type of oxygenated compounds expected to occur as surfactants has been performed by Matsuura and coauthors[76-78] on carboxylic acids, phenols, ketones and aldehydes. Their studies emphasized the interaction of the solute molecules with membranes and how these interactions affected solute permeation through the membrane.

Both positive and negative ions are repelled by cellulose acetate membranes, with water being preferentially sorbed by the membrane.[76,78,79] Sorption of neutral molecules relative to water depends on their H-bonding capacity. Strongly hydrogen-bonding compounds are attracted to the cellulose acetate membrane--some molecules pass through and others are retained in the membrane. Phenols, for example, are readily sorbed by the cellulose acetate chains.[78,80] Polyamide membranes are less polar than cellulose acetate membranes and retain less organic solutes, while yielding similar rates of organic solute separation as cellulose acetate membranes.[77]

2. EXPERIMENTAL

2.1 SAMPLE COLLECTION AND PREPARATION

2.1.1 Sample Collection

Five wellhead emulsion samples were obtained from two types of thermal oil recovery projects in Saskatchewan, namely steamflood and in-situ combustion (fireflood) projects. The steamflood projects were Canterra Energy's now-suspended Meota pilot just west of North Battleford, and Texaco Canada's Lone Rock pilot 20 km south of Lloydminster on the Alberta side of the provincial border. The in-situ combustion projects were Mobil Canada's Battrum commercial fireflood, 30 km northwest of Swift Current, Murphy Oil's Eyehill pilot, 100 km south of Lloydminster, and Mobil Canada's Fosterton N.W. pilot, just south of the Battrum field. The Meota, Lone Rock and Eyehill projects are all located in the Lloydminster heavy oil area, while the Battrum and Fosterton projects are situated in the belt of medium oil fields in the southwest corner of Saskatchewan.

Based on SRC's experience with some of these pojects--a wellhead fluid analysis program, monitoring all or most wells in the Meota, Lone Rock, Battrum and Eyehill projects, has been ongoing since 1984--and on discussions with the respective field operators, wells were selected for sampling. In the case of the firefloods, wells were chosen that were known to produce tight (difficult-to-break) water-in-oil (w/o) emulsions, the assumption being that such emulsions must be stabilized by the presence of very efficient and/or concentrated fireflood-produced surfactants. The selection of the steamflood wells to be sampled was based on the presence of oil-in-water (o/w) emulsions in the produced water phase. Brownish-coloured produced water that did not clear up after a 24-h settling period was considered to contain surfactant-stabilized o/w emulsions. Oil and grease analyses performed on arrival in the laboratory showed an oil concentration of 0.4 mg/L for the Lone Rock emulsion and an average of 4.5

mg/L for the Meota emulsion.

The five wellhead samples were obtained over an eight-month period (July 1986-March 1987). With the exception of the Fosterton sample, they were all collected by SRC staff, following special procedures aimed at reducing the possibility that the collected emulsion samples may become oxidized. In most cases, new 110-L (25 Imp. gal) drums were used, whose large bungs (the screw cap for the large filler opening) were modified to facilitate the use of the drums as feed tanks during the permeation step without having to open them again for line connections and further exposing the contents to air.

The modification consisted of one 0.95-cm (3/8") o.d.* and two 0.64-cm (1/4") o.d. stainless steel tubes, which penetrated each bung and were brazed into place. The 0.95-cm o.d. tube, equipped with a shut-off valve, served as the return line during the permeation process, while the small lines, sealed with caps during transportation, provided a means to circulate nitrogen through the drum as it was emptied during permeation. The small bung in each sample drum was replaced by a 1.91-cm (3/4") o.d. threaded pipe, equipped with a 1.91-cm, stainless steel, Kitz ball valve. This large-diameter line served as the feed line in the permeation runs. (A picture of a sample drum being used as a feed tank is shown in Figure 2.)

Prior to the sampling, in order to expel the air, the drums were completely flushed out with argon and sealed. Sampling was done by stringing a 2.54-cm (1") steam line (the temperature of the wellhead fluids varied from 100°C for the Meota and 70-100°C for the Lone Rock samples to 20-30°C for the Battrum and Eyehill fluids) from the wellhead sampling port to the drum and filling it completely. The latter prevented the sucking in of air or, if tightly sealed, the caving in of the drum that otherwise might occur on cooling. The Fosterton sample was collected by Mobil staff in a plastic, 5-gallon jerry can with no special precautions.

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*o.d. outside diameter

2.1.2 Sample Preparation

Ultrafiltration by membrane permeation of o/w emulsions at low oil concentrations (<1%) has been successfully performed by Zenon and others.[21,65-67] Membrane fouling by free oil, a potential problem of the technique, was reduced by removing surface and suspended oil prior to the runs. As ultrafiltration of w/o emulsions (as proposed for this study) had never been performed, several approaches were explored aimed at developing methods to render these emulsions amenable to membrane permeation.

Inspection of the wellhead fluids sampled in glass jars at the same time the bulk samples were collected revealed widely ranging water cuts (volume percentage of free water). The Meota and Lone Rock steamflood samples had very high water cuts (90-100%) and only a surface layer of oil. The Battrum sample had a water cut estimated at about 30%, whereas the Eyehill sample as well as the delivered Fosterton sample contained hardly any free water at all (0-10%). Therefore, different procedures had to be established to accommodate these various water cuts.

Because little oil was present in the two steamflood o/w emulsions and ultrafiltration test runs with a similar (but aged) o/w emulsion had been successful (see Section 2.2.3), they were initially subjected to ultrafiltration without special preparation. Upon their arrival in the laboratory, the sample drums were placed in a horizontal position on a specially designed cradle, with the large-diameter feed line in the lower-most position. The contents were then allowed to settle for at least 24 hours before membrane permeation was started. When membrane fouling was later suspected as being one of the factors causing poor permeation rates of fresh o/w emulsions, an oil skimming or filtration step was included before permeation was initiated (see Section 2.2.2).

As mentioned above, there was no previous experience with ultrafiltration/membrane permeation of w/o emulsions. It was obvious from the outset, however, that straightforward permeation of these emulsions through a hydrophilic membrane (the type of membrane used with o/w emulsions) would result in instantaneous and irreversible fouling of the membrane. Inversion of the w/o emulsions into low-concentration o/w emulsions appeared to be a logical approach and was pursued in a number of ways. Methods investigated were based on mechanical agitation and required the addition of water. In the case of the Battrum emulsions, free water produced by the well itself was used, whereas purified water was used with the Eyehill and Fosterton emulsions. Preliminary tests were carried out, agitating the emulsion/water mixtures with a stirrer or a blender, in combination with heating/cooling (temperature inversion), toluene dilution, or using high-pH deaerated water. Oil-in-water emulsion stability and droplet size were monitored during these experiments. Vigorous agitation with a blender proved to be the most promising approach; it produced o/w emulsions with a particle size of <1-10 µm and a stability of several hours to many days. The oil content was typically in the order of 0.4 wt %. It was also thought that this vigorous stirring would be an effective means of extracting the less water-soluble surfactants, which stabilized the original w/o emulsions, from the oil into the water phase. In order to evaluate this hypothesis and further optimize the conditions for bulk mixing of the samples, the following tests were carried out. Total organic carbon (TOC) determinations were performed to measure the amount of organic material released into the water phase. It was assumed that this material would primarily consist of the surfactants to be isolated.

Battrum

Using a blender, the Battrum emulsion sample, containing 60% water, was mixed with its own produced water (emulsion 12.6 g, water 89.2 g). The mixture was blended for six minutes and an o/w emulsion was obtained. The water phase was then filtered to remove free or suspended oil using a prefilter (Millipore HA 0.45 µm) and submitted for TOC analysis. A similarly prepared o/w emulsion was allowed to sit overnight. After this period, the water phase was almost clear with only a few large oil drops being present. Again, the water phase was filtered and submitted for TOC analysis, together with a sample of the original produced water. As the results in Table 1 show, the TOC levels were high and there were essentially no differences between the three water samples; mixing the sampled w/o emulsion in its own water did not extract or dissolve more organic material than what was already extracted in the reservoir or during production. Consequently, the same sample preparation procedures as those discussed earlier for the steamflood samples were followed, with ultrafiltration being carried out directly on the free water drawn from the sample drum.

Eyehill

The experience with the Battrum sample showed that the produced free water phase may already contain, through in-situ mixing, a maximum concentration of dissolved organic material. It was strongly suspected that the same would be true for the emulsified water entrained in a w/o emulsion. In the case of emulsion samples with hardly any free water (such as the Eyehill sample), breaking out this emulsified water could be a more efficient and convenient approach than mixing the emulsion with external water. There was a question, however, whether the oil-soluble demulsifier needed to break such emulsions would show up in the broken-out water phase and distort the results. To assess this possible interference, two samples of a primary Eyehill wellhead emulsion (labelled 1-21) were broken, one by centrifugation/heat and the other with the aid of a demulsifier. TOC measurements were subsequently performed on the separated water phases. The results (Test Series 1) are shown in Table 1, together with the TOC data on the free water phases obtained from the Eyehill fireflood emulsion (16-16) according to two methods (demulsification with a demulsifier and mixing with water). The primary emulsion data indicate that the TOC in the separated water increased when a demulsifier was used. Thus, this increase may be attributed to the demulsifier being partially soluble in water. The situation with the fireflood emulsion sample is more complicated, as the mixing method involves dilution of the organic material as well, which

Table 1. Total Organic Carbon Levels in Various W/O Emulsion Inversion and Water Separation Experiments

Sample	Test Condition	IC (mg/L)	TOC (mg/L)	TC (mg/L)
Battrum	Free (produced) water	160	1110	1270
	Immediately after blending	96	1094	1190
	24 hours after blending	77	1110	1190
Eyehill	Test Series 1			
	1-21, separated by centrifugation	250	140	390
	1-21, separated with demulsifier*	210	270	480
	16-16, mixed with 2 parts water	1	1100	1100
	16-16, separated with demulsifier*	4	6400	6400
	Test Series 2			
	16-16, mixed with 2 parts water	<1	800	800
	16-16, mixed with 1 part water	<1	1200	1200
	Bulk mixing run	2	150	152
Fosterton	Bulk mixing run	13	1133	1146

IC = Inorganic Carbon

TOC = Total Organic Carbon

TC = Total Carbon

* = Concentration used: 300 ppm

makes a comparison difficult. Theoretically, the dilution factor varies from an extreme of 3 (organic material equally soluble in oil and water) to 21 (organic material soluble in water only). As the table shows, the inorganic carbon content of the mixed and diluted sample implies a dilution factor of 4, but the error here is large.

Because of the above concern about adding a demulsifier and, more importantly, the finding that comparable quantities of organic material (taking dilution into account) were extracted by mixing with added water, it was decided to proceed with the latter approach for handling the free-water-less Eyehill and Fosterton emulsions. (As an aside to the above, it is of considerable interest to note from Table 1 that the water phase of the easily-broken primary emulsion contained 24 times less organic material than did the tight fireflood emulsion, providing a strong indication that emulsion stability may be correlated with this organic material.) Finally, a second set of experiments (Test Series 2) was conducted to determine if the concentration of the extracted organic material could be increased by reducing the volume of water being mixed in. An emulsion-to-water ratio of 1:1 proved feasible and the resulting TOC value shows that the organics concentration increased by 50% (the expected figure based on equal solubility in the oil and water phases). Thus, a 1:1 ratio was used for bulk sample preparation.

The procedure followed in bulk sample preparation was to transfer half of the emulsion out of the sample drum (under an argon blanket) and replace it with purified (reverse osmosis) water. The contents were then mixed with a barrel mixer for one hour and allowed to settle for a minimum of 24 hours. After settling, the separated water phase was transferred to a clean, empty drum filled with argon. The drum was sealed with the modified bungs and connected to the ultrafiltration unit. The much lower TOC level of the Eyehill water phase shown in Table 1 was probably due to the inefficiency of the barrel mixer, which had a circulating action rather than an agitating action.

Fosterton

The preparation method for the Fosterton sample closely followed the Eyehill procedure, except that mixing of the much smaller sample took place in a 25-L pail, allowing the use of an impeller-type mixer. Again, argon was used to prevent any contact with air. The TOC level of the resulting free water phase was among the highest encountered, proof that the mixing/extraction was efficient.

Lone Rock

As part of the work on surfactant characterization, an aging study was conducted to determine the effect of aging on the nature of emulsions. The Lone Rock wellhead emulsion was chosen as the subject for this study. Wellhead emulsion from Lone Rock well 3D4 was collected in three separate drums. The contents of one drum was subjected to ultrafiltration one day after its arrival in the laboratory, while the emulsion samples in the other two drums were allowed to stand and age one week and one month, respectively, before they underwent ultrafiltration. All three drums were kept sealed during the time they were stored.

2.2 ULTRAFILTRATION

2.2.1 Apparatus

The ultrafiltration unit consisted of a loop system comprising a feed tank, a feed pump, an ultrafiltration cell, a temperature control unit and a permeate collection container. A flow diagram is given in Figure 1.

The feed tank normally used was a conventional 110-L carbon steel oil drum with the large bung fitted, as described in Section 2.1.1, with flush gas inlet and outlet tubes and a sample return line. The sample return line extended 40 cm into the interior of the feed tank to avoid repeated sampling of the same fluid. The Kitz ball valve fitted into the small bung opening allowed the release of the feed sample from the tank into the feed pump. Figure 2 is a photograph of the sample feed tank setup. Also shown is the specially designed drum cradle, which holds the drum in a horizontal position during ultrafiltration.

The feed pump used was a CDB 1L2 Moyno positive displacement pump. A speed controller on the pump motor was installed so that regulation of the pump rate was possible. Speeds of up to 1940 rpm were possible, corresponding to a flow rate of water of more than 11.3 L/min at 25°C.

As depicted in Figure 1, a bypass loop was provided so that the feed sample could be circulated through the system while excluding the ultrafiltration cell. The flow through this bypass loop was controlled with a 0.95-cm (3/8"), Whitey stainless steel needle valve. All other valves shown in Figure 1 were 0.95-cm (3/8"), Nupro stainless steel ball valves. Pressure gauges were installed on either side of the permeation cell, allowing inlet and outlet pressure monitoring. A back pressure regulator was initially installed as shown in the flow diagram (Figure 1), but later replaced by a 0.95-cm (3/8") Whitey stainless steel needle valve. The flow

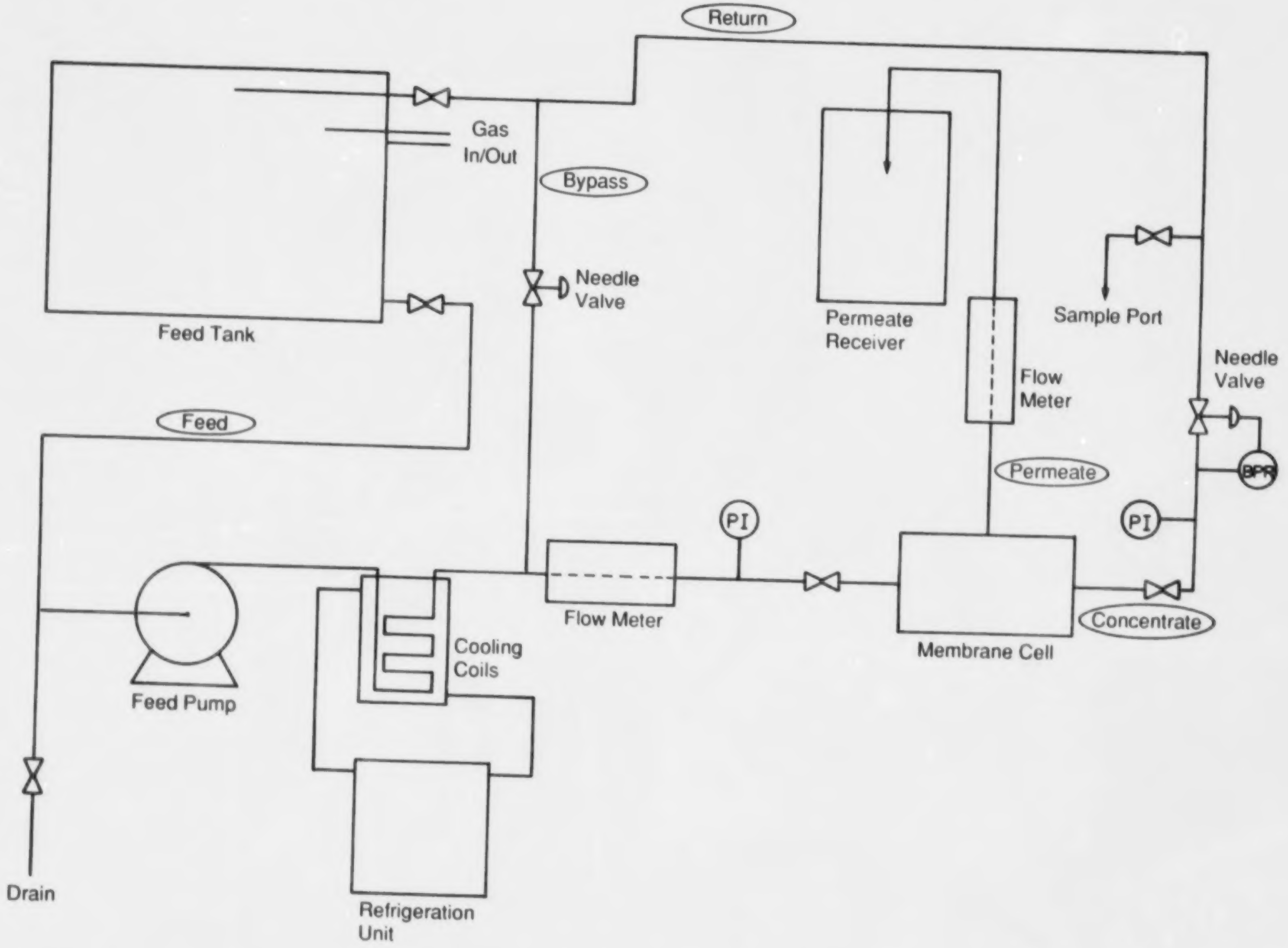
Return
Gas
In/Out
Bypass
Needle
Valve
Feed Tank
Feed
Permeate
Receiver
Flow
Meter
Sample Port
Needle
Valve
BPR
Permeate
PI
PI
Flow Meter
Membrane Cell
Concentrate
Cooling
Coils
Feed Pump
Drain
Refrigeration
Unit

Figure 1 Flow diagram of Ultrafiltration Unit

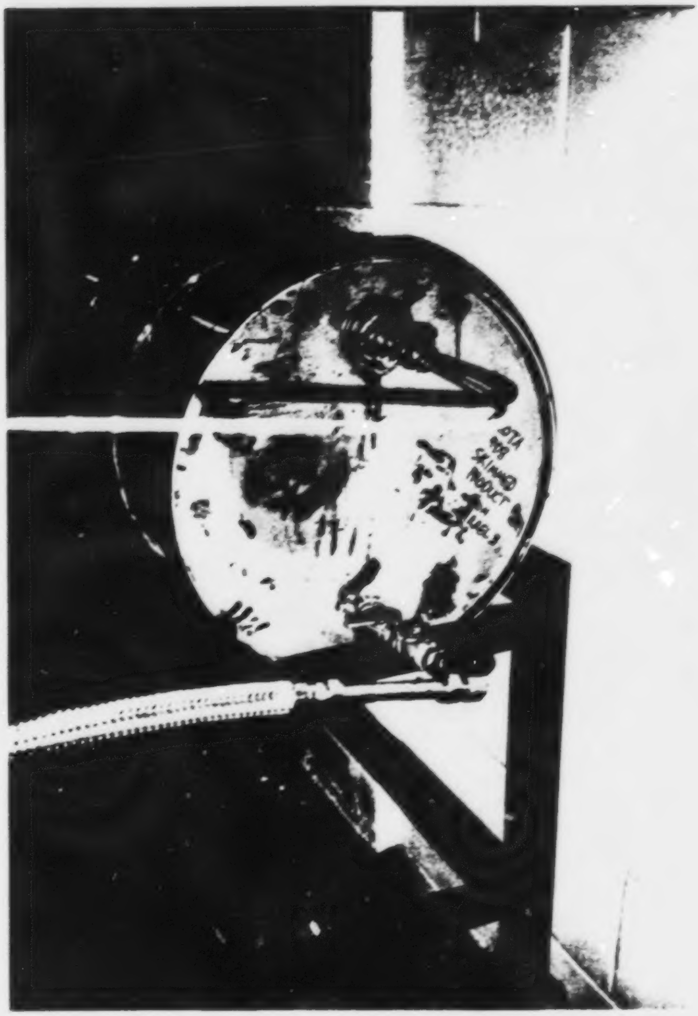
SKIMMED
PRODUCT

Figure 2. Photograph of Feed Tank Setup

rate through the ultrafiltration cell was measured with a 0.95-cm (3/8"), Hedland stainless steel flowmeter, registering flow rates from 4-20 L/min. The permeation rate was measured with a Matheson rotameter. All connecting lines consisted of 0.95-cm (3/8") o.d. tubing, except for the feedline from the feed tank to the pump (1.91 cm [3/4"] o.d.) and the permeate line (0.32 cm [1/8"] o.d.). A photograph of the ultrafiltration unit is shown as Figure 3.

The stainless steel ultrafiltration cell, designed and fabricated by Zenon Environmental, Inc., is illustrated in Figure 4. A sintered stainless steel membrane support plate allows the permeate to pass through once it has been separated by the membrane. The dimensions of the plate, and thus the effective surface area for permeation, were 5 cm x 12.7 cm (63.5 cm^2).

Initially, permeation was accomplished using Polysulfone E500 membranes, first supplied by Zenon and then by Desalination Systems. Subsequent testing of Pall Canada Nylon-66 membranes and Cellulose Nitrate membranes provided by CANMET prompted changing to the exclusive use of the Nylon-66 membranes.

The permeate was collected in 20-L glass carboys, in which a nitrogen or argon atmosphere was maintained by bubbling the gas through the permeate.

The feed tank was equipped with three barrel heaters controlled by a Variac to promote faster sample heating for ultrafiltration at elevated temperatures. Improved temperature control was further achieved by passing the loop system tubing through a temperature-regulating glycol bath. The temperature of the glycol was maintained by a Haake refrigerating and heating bath/circulator.

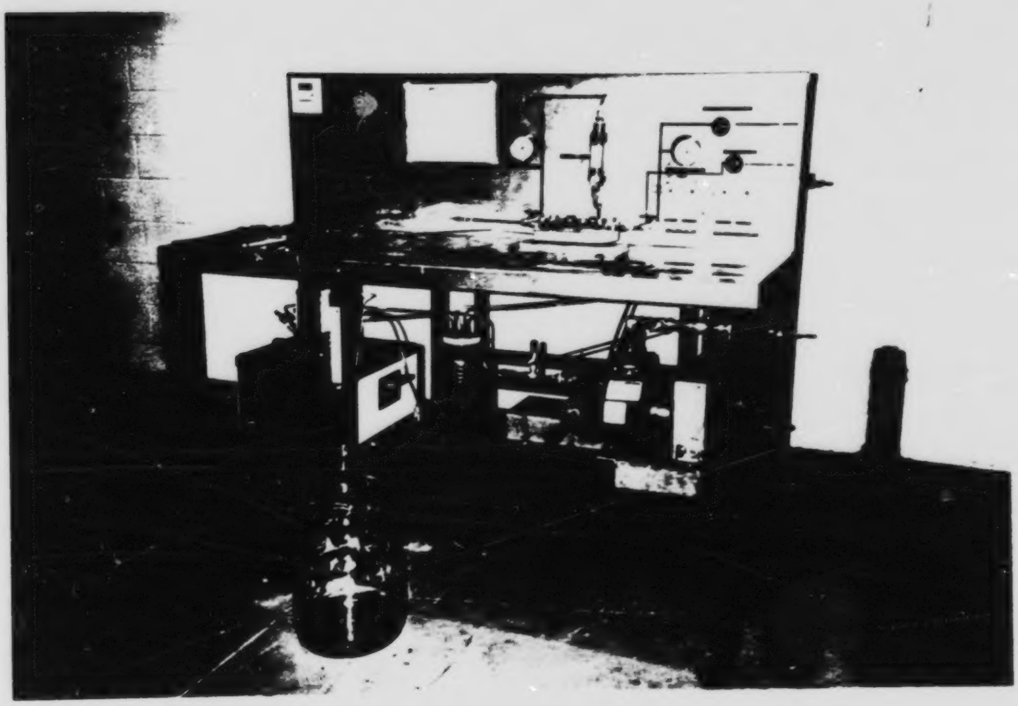

Figure 3. Photograph of Ultrafiltration Unit

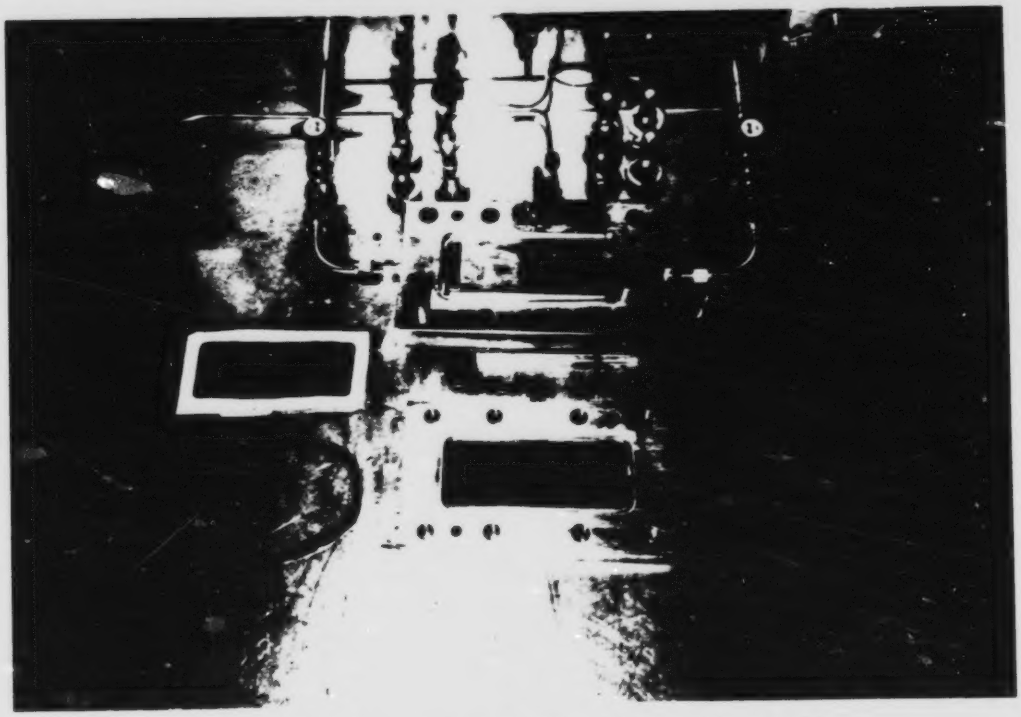

Figure 4. Photograph of Ultrafiltration Cell

2.2.2 Ultrafiltration Procedures

The carbon steel oil drums in which the emulsion samples were stored were filled to the top, thus avoiding contact with the atmosphere once filled. If the modified bungs with gas inlet/outlet lines and sample inlet/outlet lines were not already attached in the field, they were installed under a flow of argon to minimize air exposure. Since the samples were stored with the drums in vertical position, a minimum period of one hour was allowed for the oil/emulsion layer to settle, when a drum was loaded onto the above-shown drum cradle in preparation for ultrafiltration. This minimized the amount of free oil in the water phase drawn from the feed tank.

Old sample was flushed from the system lines by pumping fresh sample through with the sampling valve left open. The sample was then allowed to circulate, while bypassing the permeation cell, for five minutes. After this period ultrafiltration was initiated.

The initial operating conditions were:

- flow rate of 10.6 L/min (measured with tap water at room temperature)
- 550 kPa inlet pressure; 450 kPa outlet pressure
- fresh Polysulfone E500 membrane (supplied by Zenon)
- 60°C operating temperature

As a result of the various test runs described in Section 2.2.3, these conditions were later modified to:

- operate at room temperature
- exclusive use of Nylon-66 membranes (pore size 0.2 μm)

Also based on the test results of Section 2.2.3, the following additional procedures were established and performed in all pertinent preparative runs.

Oil Skimming Procedure - When the amount of free oil in an o/w emulsion sample prohibited ultrafiltration because of extensive fouling of the membrane, the free oil was removed from the sample. The lower layer of the sample containing the o/w emulsions was allowed to drain through paper towels used as a filter into another drum sample below. Argon gas was bubbled into the collecting drum throughout the procedure to minimize exposure to air.

Sintered Plate Cleaning Procedure - The procedure developed for unplugging the sintered stainless steel plate in the ultrafiltration cell was as follows: the plate was successively washed with varsol, acetone and then water until the flow rate through the plate reached 30 mL/min under atmospheric pressure. A reverse flow of air was then forced through the permeate line and plate to ensure no blockages remained.

2.2.3 Optimization of Ultrafiltration Conditions

Based on the procedures and conditions established by Zenon[21] for the ultrafiltration of low-concentration o/w emulsions, a number of preliminary permeation runs using seven-month old (aged) Meota o/w emulsions were conducted to confirm these conditions. Although these runs did not point to any potential problems, serious difficulties (i.e. zero permeation rates) were encountered when attempts were made to perform ultrafiltration of fresh o/w emulsions. It was thus necessary to re-evaluate, through test runs, various procedures and operating conditions (including different membranes), before routine ultrafiltration of fresh samples could be performed. The observations and results of all relevant test runs are summarized below.

- Determination of Initial Operating Conditions Using Tap Water

The flow rate was determined by running the feed pump at its optimum of 1420 rpm. This rotational speed corresponded to a flow rate of 10.6

L/min using tap water at room temperature. Various inlet pressures were measured at this flow rate using tap water at room temperature. The permeation rate increased as a function of increasing inlet pressure up to a pressure of 550 kPa. The permeation rate then remained constant as the pressure was further increased. Thus, 550 kPa was identified as a suitable operating inlet pressure. The corresponding pressure at the outlet of the ultrafiltration cell was measured as 450 kPa.

Zenon found an increased permeation rate for ultrafiltration of o/w emulsions at a temperature of 60°C compared to room temperature.[2] Although the experiments with tap water yielded no increase in flux rate at temperatures of 60°C compared to room temperature, operating temperatures of 60°C were used for the initial experiments.

Using the operating conditions of 10.6 L/min flow rate, 60°C operating temperature, 550 kPa operating pressure and the fresh Polysulfone E500 membrane supplied by Zenon, the initial permeation rate was measured as 18.1 m^3/m^2.day. This value decreased as a function of run time to a minimum value of 8.4 m^3/m^2.day.

- Ultrafiltration of (Previously Sampled) O/W Emulsions

The first ultrafiltration runs using o/w emulsions were performed on two samples collected seven months previously from Meota wells 4D8 and 3D8. No special precautions were taken to prevent oxidation of these emulsions. The sample from well 4D8 was determined at collection time to have an oil and grease concentration of 1.22 wt %, which had dropped to 0.07% at the time of ultrafiltration. The permeate flux rate was initially measured as 19.3 m^3/m^2.day, but it dropped to 5.0 m^3/m^2.day after one hour. The flux rate remained stable at this level for seven hours. A sample with a higher oil and grease concentration (well 3D8) was measured at 9.8 wt % oil and grease after collection, and 0.75% oil and grease at the time of ultrafiltration. Permeation of this sample was performed with a used membrane, yielding an initial flux rate of 6 m^3/m^2.day, falling to 0.4 m^3/m^2.day after three hours. After changing the membrane, the initial permeation rate of 10.8 m^3/m^2.day fell to 1.9 m^3/m^2.day in four hours.

• Ultrafiltration of Fresh O/W Emulsions

Very poor permeation rates were obtained for the ultrafiltration of fresh o/w emulsions, collected from Meota wells 4D8 and 3D8 one day before the experiments. Meota 4D8 had a measured oil and grease concentration of 4.5 wt % and yielded an initial flux rate of 0 m^3/m^2.day (run 4). The membrane was found to be completely oil-fouled and, when changed, a flux rate of 0.2 m^3/m^2.day was obtained for less than 0.3 hours.

The sample from Meota well 3D8 containing 0.50 wt % oil and grease was stored in an air-free atmosphere and then subjected to ultrafiltration 16 days later (run 5). An initial flux rate of 0.2 m^3/m^2.day was obtained, dropping to 0.1 m^3/m^2.day after 1.4 hours. The membrane was not visibly oil-fouled.

Because of the very poor permeation rates, collection of sufficient permeate for analysis was obviously impossible. The following parameters were then tested in an attempt to improve ultrafiltration performance.

a) Membrane Source

Ultrafiltration of tap water showed that no permeation occurred for any runs using membranes cut from one of the two Zenon sheets (Polysulfone E500). These membranes were used for the above run with Meota 4D8 (run 4). All subsequent runs employed Polysulfone E500 membranes obtained from Desalination Systems, which yielded good permeation rates for tap water.

b) Removal of Free Oil From Sample

After visual inspection of the membranes used in many trial runs with

Meota 4D8 had shown complete oil fouling, a procedure was initiated to remove free oil from the sample as outlined in Section 2.2.2. This procedure was performed for several trials on Meota 4D8, and no oil fouling of the membranes was detected. Unfortunately, low flux rates (run 7) were still obtained (0.2 m^3/m^2.day, stable for one hour).

c) Exposure of Permeate to Air

The hypothesis was proposed that the low permeation rates of fresh emulsion samples were caused by components in the permeate being oxidized by exposure to air (on the permeate side of the membrane) and precipitating out of the solution, thereby plugging the membrane pores. To test this hypothesis, the cell system and permeate lines to the collection flash were flushed with nitrogen prior to ultrafiltration (run 8). The emulsion sample used was skimmed Meota 4D8 (see [b] above) and room temperature operating conditions were maintained. An adequate flux rate of 6.5 m^3/m^2.day, decreasing to 6.0 m^3/m^2.day after 1.3 hours was obtained.

As a double check of this theory, a second trial using the same emulsion was conducted under identical operating conditions, except that the cell was not flushed with nitrogen (run 9). Again, an improved permeation rate of 8.3 m^3/m^2.day, decreasing to 6.6 m^3/m^2.day in 0.7 hours, was obtained. Because this result did not support the oxidation theory, it was thought that the success of the last two runs (8 and 9) could be due instead to operating at room temperature rather than the usual 60°C.

d) Operating Temperature

Using the skimmed Meota 4D8 emulsion again and the used membrane from run 9, ultrafiltration was performed under the same conditions as in run 9, but at an operating temperature of 52°C (run 10). The flux rate obtained was 5.2 m^3/m^2.day, thus indicating that the lack of success in previous runs with fresh emulsions (runs 4, 5 and 7) was not due to running at high temperatures. Nevertheless, since operating at elevated temperatures did not appear to improve the flux rate, it was decided to perform all successive runs at room temperature.

e) Plugging of Cell System

Several more ultrafiltration runs with fresh emulsions were performed, with generally decreasing success and confusing results. None of these runs yielded the permeation rates required for collecting the amount of permeate necessary for analysis. When a sample of tap water was rerun as a check on the system, no permeation occurred. It was then discovered that the sintered steel plate of the ultrafiltration cell, which supports the membrane, was plugged and permitted no permeate to flow through. After adopting the cleaning procedure outlined in Section 2.2.2, a permeation rate of 6.7 m^3/m^2.day was obtained.

In retrospect, the fact that the plate was plugged could likely have been the reason for the poor permeation flux rates obtained in runs 5 and 7 and, possibly, in other runs. The nitrogen flushing of the cell in run 8 may have cleared the pores in the plate, allowing good permeation rates for runs 8, 9 and 10. Unfortunately, this factor alone does not completely explain the success or lack of it in various runs. The following is a good example of this.

Ultrafiltration of fresh Meota 3D8 with a cleaned sintered plate gave a flux rate of 1.9 m^3/m^2.day, decreasing to 1.0 m^3/m^2.day in 4.2 hours. Ultrafiltration of the same emulsion after one day of air exposure, using a fresh membrane but not having cleaned the plate after the previous run, yielded an initial flux rate of 5.0 m^3/m^2.day. One possible explanation for the improved permeation rate after air exposure and settling of the emulsion would again involve the precipitation of components after oxidation. If these emulsions are not exposed to air until they enter the cell, oxidation of permeate components followed by their precipitation would initiate plugging of the sintered steel plate. In contrast, if the samples are exposed to air prior to ultrafiltration, elapsed time would allow the oxidized components to precipitate out harmlessly in the storage tank.

Oxidation and settling apparently reduced the amount of oil fouling experienced as well. Ultrafiltration runs of fresh Meota 4D8 emulsion (run 4) that had never been exposed to air gave prohibitive oil fouling in five minutes with three different types of membranes. When fresh Meota 4D8 emulsion that had undergone repeated ultrafiltration runs and had been exposed to air was run once more, a good permeation rate with no oil fouling of the membrane was obtained. This suggested that the combination of exposure to air, pumping and circulation during ultrafiltration, and long settling times prevented oil fouling.

f) Membrane Type

Using the oil skimming procedure under the exclusion of air outlined in the procedure section (2.2.2), the free oil was removed from fresh Meota 4D8 emulsion that had not been exposed to air. This skinned emulsion was then used in testing the three types of membranes listed below.

Membrane	Pore Size (µm)	Permeation Rate (m^3/m^2.day)
Polysulfone E500	0.04	1.0 decreasing to 0.4 in 1.3 hours
Cellulose Nitrate	0.01	0.1 increasing to 0.2 in 0.4 hours
Nylon-66	0.1	3.5 decreasing to 2.4 in 0.5 hours[1]
		2.9 decreasing to 2.0 in 0.5 hours[2]
Nylon-66	0.2	16.5 decreasing to 2.8 in 7.4 hours (stable at 3.4 for 5.5 hours)

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[1] Because of emulsion leaking through this membrane, the permeation rates were estimated by measuring the visible light absorbance of the collected permeate.

[2] Estimated values.

Because of the higher permeation rates achieved and the possibly better separation characteristics of the Nylon-66 (0.2 µm) membrane (this membrane is more hydrophilic than Polysulfone), it was decided to use the Nylon-66 0.2 µm membrane for all successive ultrafiltration runs.

2.3 ISOLATION OF SURFACTANTS

As described in Section 2.2.2, all permeates were collected in 20-L carboys, while using argon to provide an oxygen-free atmosphere in the collecting vessel. The initial permeate appearances varied from clear and colourless to clear pale-yellow. While the ultrafiltration runs progressed, or on standing, most permeates changed to a darker colour (Meota 4D8 dark orange/purplish brown; Lone Rock 3D4 orange to dark purple; Battrum 7-26 yellow/cream; Fosterton cloudy orange). Moreover, a large amount of an orange-brown precipitate settled on the bottom of the carboys containing the Battrum permeate. It is significant to note that the colour changes also occurred in the permeates collected from the "aged" Meota emulsions used during the initial trial runs. No special precautionary measures (e.g. inert gas blanketing) were taken to protect these emulsion samples from oxidation, although the permeates from these samples were collected and stored under nitrogen.

A brief investigation into the causes of these colour changes was conducted. Possible causes were considered to be oxidation, effects of light and temperature, chemical reactions and oil breakthrough. Tests with small quantities of a Lone Rock permeate exposed to combinations of air/no air/light/no light conditions revealed that air exposure was definitely a factor. Oil penetration through the membrane was ruled out and it was also determined that light and temperature had no effect on the colour changes. The use of argon instead of nitrogen as the inert gas bubbling through the permeate did slow down the rate of colour change, but could not stop it. The type of membrane used for ultrafiltration also appeared to have an effect. Fresh Meota 4D8 o/w emulsion permeated through a Nylon-66 0.2 μm membrane produced a clear yellow solution, while the permeate from a Polysulfone membrane was clear brown/pink. Because no causes for the colour changes could be explicitly identified, no special procedures were followed during permeate collection other than maintaining an argon overpressure in the collection vessels (see also Section 2.3.2).

The original work statement listed three methods to be used for the isolation of the surfactants from the permeates: (i) freeze-drying; (ii) acidification/precipitation and ethyl acetate extraction of water-phase supernate; and (iii) preparative reverse phase chromatography. During the processing of the first two emulsion samples (Lone Rock and Meota) both experimental and practical difficulties led to various procedural modifications, which were implemented in consultation with the Scientific Authority. These changes are described below. At the same time, the original characterization schedule associated with the various isolation procedures also had to be revised. Details of this are given in Section 2.4.

2.3.1 Water Phase Removal

After permeation was completed, a small sample of the raw permeate was collected for analysis. The remainder of the permeate was then used for surfactant isolation. The first isolation method specified in the work statement was freeze-drying. Since it was expected that several litres of permeate would have to be dried in order to obtain sufficient surfactant material and SRC did not have an adequately-sized freeze-dryer, the National Research Council (NRC) laboratory in Saskatoon was requested to perform the freeze-drying in their large units. Three permeates (Lone Rock unaged, aged one week, and aged one month) were submitted for freeze-drying by transferring the aqueous phase under nitrogen into sealed, 0.5-L aluminum foil trays, immediately deep-freezing these trays, and shipping them to Saskatoon in insulated containers. Eleven to eighteen trays were used for each permeate. The freeze-dried products consisted of fluffy pink to pink-brown flakes.

Because of the complications involved in the preparation and shipment of the samples as well as the considerable amount of turnaround time required, the feasibility of water removal by rota-evaporation was investigated. The permeate was transferred (0.5 L at a time) under nitrogen to a round-bottom flask and the water was removed using a Büchi Rotovapor R110 at temperatures of 50-60°C and moderate vacuum. A comparison by infrared spectroscopy of the products obtained by freeze-drying and rota-evaporation did not reveal any significant differences. Consequently, the rota-evaporation method for water removal was used for all remaining permeates. Typically, rota-evaporation of approximately 500 mL of permeate provided enough dried product (≈ 1 g) for the subsequent elemental and infrared (IR) analyses.

2.3.2 Acidification/Precipitation and Solvent Extraction

The second surfactant isolation procedure called for acidification of the permeates, followed by filtration of the generated precipitate and extraction of the organic material remaining in the filtrate with ethyl acetate.

The first step of this procedure, acidification of the permeate was performed without complications. Permeates were acidified with concentrated hydrochloric acid to pH 2, a low enough value to insure complete protonation of all organic acids. Interestingly, acidification had the unexpected side-effect of causing the colour of the permeates to change back to their usual pale-yellow starting colour. This may indicate that the observed colour changes on standing might have been due to acid and base forms rather than oxidation per se. Also upon acidification, the murkiness and most of the red-brown precipitate in the Battrum permeate disappeared. This precipitate was believed to consist of iron oxide compounds. Indeed, iron analyses on the permeates obtained from the same Battrum sample drum over a one-month interval showed an increase from 14.6 to 65.8 mg/L iron, which was attributed to corrosion of the sample drum.

Acidification was expected to generate a precipitate, which was to be separated by filtration. However, hardly any precipitate was formed in any of the permeates; only in the Lone Rock and Meota permeates a flaky brown or fine black precipitate was observed several hours after acidification. Attempts were made to recover this material by filtration, but the amounts recovered were too small to permit any analyses other than IR. In consultation with the Scientific Authority it was, therefore, decided to omit the precipitation/filtration step and to directly proceed with the ethyl acetate extraction of the acidified permeates.

Aliquots of 1250-mL acidified permeate were extracted with ethyl acetate in a two-litre separator funnel. Typically, three extractions of 150 mL, 100 mL and 50 mL were required for a single aliquot to render the ethyl acetate layer clear and colourless. In some cases, more extractions were needed (e.g. the Battrum permeate required six extractions). The ethyl acetate layer was then passed through a sodium sulphate filter and transferred into a round bottom flask for rota-evaporation. The ethyl acetate was removed in a Büchi Rotavapor R110 at 30°C under moderate vacuum.

In order to collect the oily or solid product left in the drying flask, it was necessary to add a small amount of ethyl acetate and redissolve the residue. This solution was then pipetted into a vial and placed in a vacuum desiccator for final removal of the solvent. The ethyl acetate-extracted products had a pasty appearance and were yellow to brown/black in colour. They were subjected to various characterization methods described in Section 2.4. A minimum of 20-40 L of permeate had to be extracted to yield enough material (≈ 2 g) for these analyses. The organics content of the permeate as determined from the TOC measurements served as a guide in determining the volume of permeate required.

2.3.3 Chromatographic Separation

The original work statement listed preparative reverse phase chromatography as the third method for isolating the surfactants. Syncrude Research had used this type of chromatography for the characterization of organic substances in their aqueous waste streams. The method employs a reverse phase adsorbent that retains the organics from an aqueous phase, while rejecting water and dissolved salts. A copy of the procedure, detailing the various steps, was obtained from Syncrude Research.

An alternative approach, consisting of preconcentrating the organic solutes on a column and separating them into three general classes (acidic, basic and neutral),[81,82] was then proposed by SRC for two main reasons. First, this approach should result in a better recovery efficiency and, second, it should provide more information as the various compound classes will be characterized separately. In addition, the approach will allow a possible further separation according to chemical functional groups (e.g. alcohols, esters, acids, nitrogen compounds, etc.), if so desired. Following the approval by the Scientific Authority, the recommended procedure was implemented.

As the flow chart (Figure 5) shows, the procedure started with acidification of the feedstock (raw permeate) to pH 2. Again, hydrochloric acid was used for acidification. The acidified aqueous phase was then passed through a chromatographic column, packed with purified polystyrene-divinylbenzene resin (Bio-Beads), which acted as an adsorbent for the organic solutes. The aqueous effluent was collected. The organic phase retained on the resin was then eluted, in three steps, with 250 mL 0.10 M NaOH to obtain the acidic compounds, 250 mL 1.0 M HCl to obtain the basic compounds, and 250 mL HPLC-grade methanol to obtain the neutral compounds. The aqueous effluent from the first phase was then adjusted to pH 12 with concentrated NaOH and passed through another column packed with purified polystyrene-divinylbenzene resin. The organic solutes retained on this column were eluted, in two steps, with 1.0 M HCl and HPLC-grade methanol. This second pass was performed in order to recover any basic or neutral compounds that may have been present in the effluent from the first pass.

It is of interest to note that increasing the pH of the effluent from the first pass to pH 12 caused precipitates in the Battrum, Eyehill and Fosterton cases. Whereas the acidified Eyehill permeate had been clear and

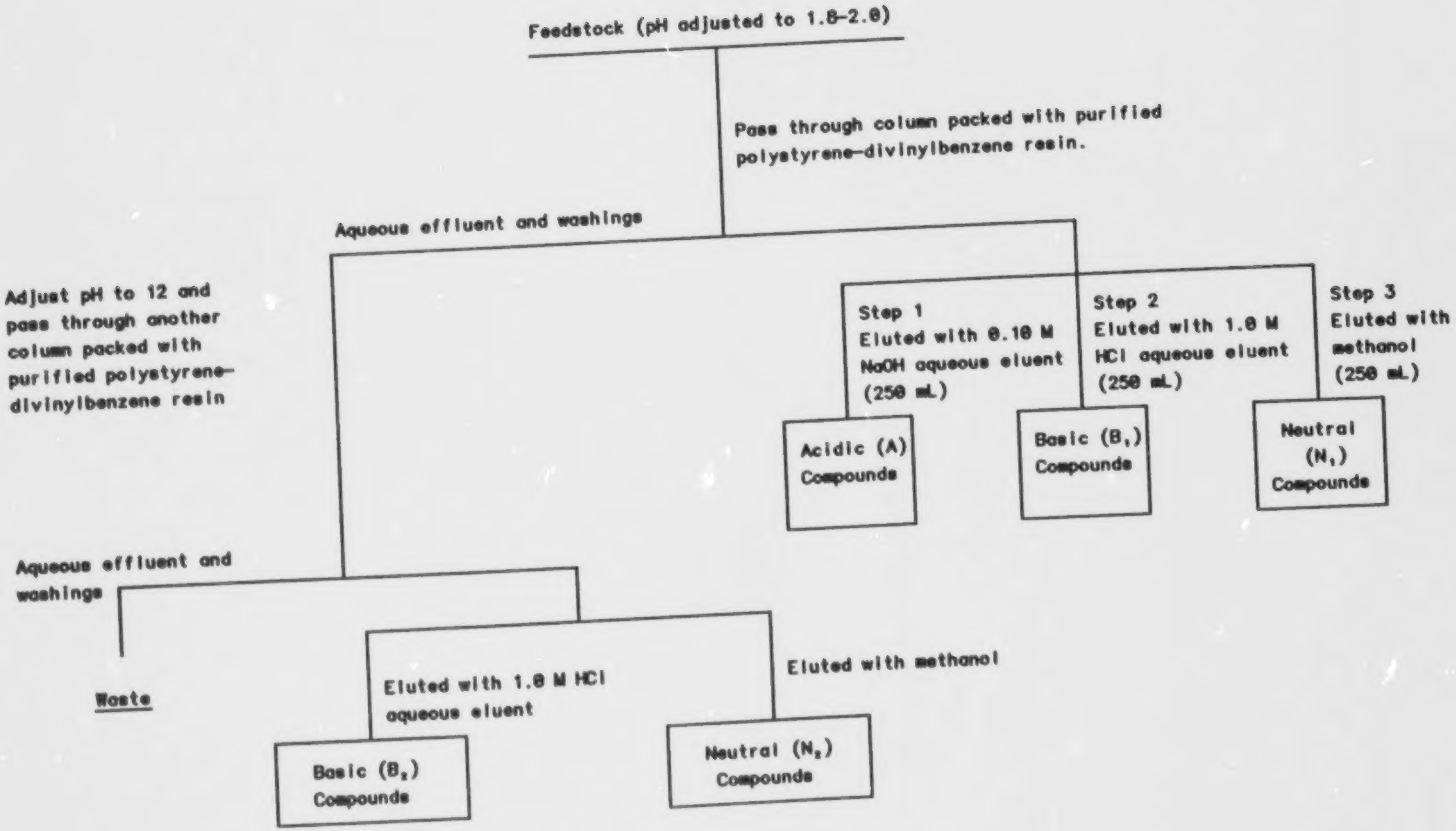
Feedstock (pH adjusted to 1.0-2.0)
Pass through column packed with purified polystyrene-divinylbenzene resin.
Aqueous effluent and washings
Step 1
Eluted with 0.10 M NaOH aqueous eluent (250 mL)
Acidic (A) Compounds
Step 2
Eluted with 1.0 M HCl aqueous eluent (250 mL)
Basic (B₁) Compounds
Step 3
Eluted with methanol (250 mL)
Neutral (N₁) Compounds
Adjust pH to 12 and pass through another column packed with purified polystyrene-divinylbenzene resin
Aqueous effluent and washings
Waste
Eluted with 1.0 M HCl aqueous eluent
Basic (B₂) Compounds
Eluted with methanol
Neutral (N₂) Compounds

Figure 5. Flow Chart of Extraction of Organic Species in Aqueous Medium by Column Chromatography

colourless, the addition of NaOH to the effluent from the first pass caused the water to turn cloudy and orange-brown coloured, with a dark green-black precipitate settling on the bottom of the tank. A second layer of orange precipitate was formed after standing for some time. These precipitates were not soluble in organic solvents, but did dissolve in diluted hydrochloric acids. Similar observations were made with the Battrum and Fosterton effluents. Increasing the pH to 12 caused fluffy, orange-yellow or dark green-black precipitates to form, while the water phases turned clear and colourless. All these precipitates were believed to be iron hydroxides.

The experimental setup consisted of a 20-L glass feed tank (a carboy), a double, 10-mm i.d.*, pressure-type glass column (SR10/50) with an effective length of 500 mm, and a 20-L glass collecting tank. The feed tank, and hence the column, was pressurized with argon to increase the flow rate through the column. This made it possible to pass volumes of acidified permeate, typically varying from 10 to 40 L, through the column in one to three days.

A total of 25 fractions, each ranging from 250-500 mL in volume, were collected according to the above procedures. As shown in the schedule of analytical determinations (Table 2), these fractions were subjected to IR and GC/MS analyses. While the GC/MS equipment could handle aqueous or methanol-dissolved samples, IR analyses could only be performed on water-free samples. Thus, the water phases as well as any methanol had to be removed, which was accomplished by freeze-drying and drying in a vacuum oven at 40°C. Since the high mineral salt concentrations in the solid residues would interfere with the IR analyses on these solids and the acidic and basic organic compounds present in the solids would be analyzed as organic salts, a further extraction was performed using small amounts of acidified methanol and basic methanol to extract the acidic and basic organic compounds, respectively, in their neutral form. The dried neutral fractions were extracted with a mixture of methanol and carbon tetrachloride. These extractions were repeated three to four times and the solvents were subsequently removed by vacuum evaporation.

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*i.d. inside diameter

2.4 PRODUCT CHARACTERIZATION

The products and fractions isolated according to the procedures described in Section 2.3 were subjected to a comprehensive array of analytical characterization methods. Various changes were made to the original schedule of determinations, partly because of changes in the isolation procedures (no precipitates at low pH, modified chromatographic method), partly because some originally proposed analyses were impractical (e.g. too low concentration, too much salt), or not feasible (e.g. product insoluble in water). A revised schedule of analytical determinations, reflecting the analyses actually performed, is shown in Table 2. Details of the procedures followed and the equipment used for each of these analyses are discussed below. All analyses were performed at SRC, unless indicated otherwise.

2.4.1 Acid-Base Titrations/Acid Number Determination

Acid-base titrations were performed on the raw permeates. A Metrohm E636 autotitrator, employing a glass (EA109) and a saturated calomel (EA404) electrode pair, was used to perform the titrations. The titrant for the acid titrations was 0.1 M hydrochloric acid, which was standardized daily against tris-(hydroxymethyl) aminomethane (THAMN). The base titrations were performed with 0.02 M potassium hydroxide, which was standardized against potassium hydrogen phthalate. The permeates were titrated using the dynamic titration mode to inflection endpoints.

Since the ethyl acetate extracts were insoluble in water, regular titrations on these extracts could not be performed. Instead, a modified version of the ASTM D664 titration procedure was used to determine the total acid content (acid number) of the extracts and to provide a breakdown

Table 2. Schedule of Analytical Determinations

Method Fraction	a	b	c	d	e	f	g	h	i	j	k
Raw permeate	+		+	+	+			+			
Dried permeate		+							+		
Dried water phase after extraction		+									
Ethyl acetate extract	+	+				+	+		+	+	+
Organics chromatography (acidic, neutral, basic fractions)									+		+

a) Titrations (acid and base)

b) Elemental analysis of solids: C, H, N, O, S

c) Analysis of aqueous samples: TOC

d) Metals (Mg, Ca, Na, K, Fe), Cl and Si

e) Phenols

f) Thermal gravimetric analysis

g) Vapour phase osmometry

h) Interfacial tension

i) IR

j) ^{13}C NMR

k) GC/MS (mass sensitive detector)

into very strong (mineral and sulfonic acids), strong (carboxylic acids) and weak (Lewis acids, phenols) components.[83] The extracts were first dissolved in a mixture of 80% methanol and 20% carbon tetrachloride, and then titrated in a mixture of toluene, water, isopropanol and tetrahydrofuran (50.0 : 0.5 : 24.5 : 25.0). The titrant was 0.05 M potassium hydroxide in isopropanol, which was standardized as described above.

2.4.2 Elemental Analysis (C, H, N, S)

Elemental analyses were performed on the dried permeates, the ethyl acetate extracts and the dried residues from the water phases after extraction. The latter analysis served as a check on the efficiency of the ethyl acetate extraction. Carbon and hydrogen contents were determined using a Perkin Elmer Model 240C elemental analyzer, sulfur using a Leco Sulfur Determinator SC32 and nitrogen using an Antek 720/771 Nitrogen Detector.

2.4.3 Total Organic Carbon Determination

Total organic carbon (TOC) measurements were made on the free or o/w emulsion-containing water phases (before the ultrafiltration runs) and on the raw permeates, using a Beckman TOC analyzer.

2.4.4 Anion and Cation Determination

The determination of the concentrations of the inorganic ions was performed on the raw permeates only. Metal ion (Mg, Ca, Na, K and Fe) concentrations were determined using a Hitachi 180-80 atomic absorption spectrometer.

The chloride concentration was determined according to the ASTM D512 (method B: silver nitrate titration) procedure.

Siliceous compounds in the permeates were determined as silicon by atomic absorption (ICP and AA).

2.4.5 Phenols Determination

The concentration of phenols in the raw permeates was determined according to Method 510C (Direct Photometric Method) of "Standard Methods for the Examination of Water and Waste Water" (15th Edition, 1980), published by the American Public Health Association, the American Water Works Association and the Water Pollution Control Federation. The method is based on the reaction of phenolic compounds with 4-amino antipyrine in the presence of ferricyanide to form a coloured dye, whose absorbance is determined at 500 nm.

2.4.6 Thermogravimetric Analysis

Thermogravimetric analysis was performed on the ethyl acetate extracts in order to obtain information on the thermal stability of the isolated organic materials. The equipment used was a DuPont 951 thermogravimetric analyzer. The sample size used was ≈17 mg. Samples were heated from 40°C to 800°C at a standard heating rate of 10°C/min in a nitrogen stream flowing at 58 mL/min. The weight loss versus temperature data were continuously collected by a DuPont Model 1090 Data Analysis System, which reproduced the thermal trace and its time derivative on the same graph.

2.4.7 Vapour Pressure Osmometry

The vapour pressure osmometry technique was used to determine the average molecular weight of the ethyl acetate extracted materials. The determinations were performed by the Department of Chemistry, University of Alberta, Edmonton, Alberta, using a MechroLab 301A vapour pressure osmometer and pyridine as the solvent.

2.4.8 Interfacial Tension

Measurements of the interfacial tension (IFT) between oil and water phases were performed on the raw permeates, using a 'neutral' oil as the reference oil. This neutral oil was a lubricating oil base stock, obtained from the Consumers' Cooperative refinery in Regina. The originally scheduled IFT measurements using the ethyl acetate extracts as surfactant could not be performed because of the inability of the extracts to redissolve in water. Because this insolubility of the extracts excluded the possibility of directly measuring the effects of these isolated organic materials on the IFT, additional IFT measurements were needed to better estimate the contribution by these materials to the measured IFT as they were dissolved in the raw permeates. Interfacial tension is very sensitive to the presence of any dissolved substance. Given the high levels of dissolved solids in most permeates, data were first needed to assess the effect on the IFT by these dissolved solids. Thus, two synthetic brine solutions were prepared to simulate a low (5400 ppm) and a high (58,550 ppm) TDS (total dissolved solids) permeate. These TDS levels reflected the Lone Rock and Eyehill permeates, respectively, and so did the relative amounts of the various salts used (KCl, $NaCl$, Mg_2SO_4 and $CaCl_2$). The IFT of these brine solutions was measured against the neutral oil and compared with the IFT of pure deionized water.

Other IFT measurements performed for comparative purposes included those of a water-free Lone Rock oil in Lone Rock raw permeate, the same Lone Rock oil in deionized water with a surfactant added (0.01 wt % SRC-K1), and the neutral oil in deionized water with surfactant (0.01 wt % SRC-K1) added. The surfactant SRC-K1 was used as an example of an efficient emulsifier, known to produce stable o/w emulsions. The magnitude of the IFT reduction achieved with SRC-K1 served as a measure for comparison with the actual raw permeate IFT data.

The equipment used for the measurement of the interfacial tension was a SITE LP-10 spinning drop interfacial tensiometer. Its principle of operation is based on the phenomenon that a drop or bubble placed in a capillary tube containing a second, more dense phase elongates and eventually assumes a static, elongated shape, when the capillary tube is rotated about its longitudinal axis at high speeds. The equilibrium configuration achieved results from a balancing of centrifugal forces causing the elongation and interfacial forces resisting the elongation. Hence, by measuring the centrifugal force effect, the interfacial tension is determined. The IFT is actually calculated from the length of the drop, its radius, the density difference between the two phases and the rotational speed. Rotational speeds from 5000-10000 rpm were required; the temperature was 20°C for all determinations. The drop was allowed to equilibrate until successive readings were consistent.

2.4.9 Infrared Analysis

Infrared (IR) analyses were performed on the dried residues left behind after removal of the water (by roto-evaporation or freeze-drying) from the raw permeates and from the water phases after ethyl acetate extraction, on the ethyl acetate extracts and on all chromatographically separated fractions (acidic, neutral and base fractions).

The dried permeate and water phase residues contained usually enough salt to permit the preparation of a sample pellet without the addition of potassium chloride. If a sample was too concentrated (as seen from the IR spectrum), potassium chloride was added to reduce the concentration of the sample. The ethyl acetate extracts were run by redissolving them in a small mount of ethyl acetate, applying this solution to a potassium chloride salt plate and allowing the solvent to evaporate under vacuum. As described in Section 2.3, the chromatographic fractions underwent further drying and extraction steps in preparation of their analysis by IR. The extraction steps yielded methanol and methanol/carbon chloride solutions, which were applied to a salt plate and dried under vacuum.

The infrared spectra were recorded on a Perkin Elmer 683 infrared spectrophotometer.

2.4.10 ^{13}C NMR Spectroscopy

Carbon-13 NMR spectroscopy was performed on four ethyl acetate extracts (Meota was not included due to insufficient sample). Solutions for the measurement of the ^{13}C NMR spectra were prepared by dissolving each of the ethyl acetate extracts (Battrum 0.4 g, Eyehill 0.5 g, Fosterton 0.5 g and Lone Rock 0.6 g) in 2 mL of deuterated dimethylsulfoxide (DMSO-D_6, 99% d), containing 80 mg chromium(III) tris-acetyl acetonate [Cr(Acac)$_3$] as the relaxing agent. The solvent and the relaxing agent were supplied by Aldrich and used without further purification.

Carbon-13 NMR Fourier transform (FT) spectroscopy was performed at the University of Alberta on a Bruker WH 200 superconducting, high-resolution NMR spectrometer, operating at 50.323 MHz and using a 20-mm broadband probe insert. Experimental conditions were: sweep width, 15000 Hz (≈300 ppm); dwell time, 33.3 μs; memory size used for data acquisition, 16K words; digital resolution, 1.8 Hz; acquisition time, 0.54 s; pulse width, 28 μs (90° flip angle); pulse sequence delay time, 2 s; number of pulses, varying from 2000 to 3300; FT line broadening, 2 Hz; sample tube diameter, 10 mm; sample temperature ambient; internal deuterium field-frequency lock using the deuterium signal of the solvent; and internal frequency standardization using the ^{13}C signal of the solvent as the reference signal. Gated broadband proton decoupling at 200 MHz was performed using a NONOE program to suppress the nuclear Overhauser effect (NOE).

An attempt was also made to perform ^{13}C NMR on two chromatographic fractions. Overnight runs, using the Bruker WH200 spectrometer for the Battrum acidic fraction and a Bruker AM300, operating at 75 MHz, for the Lone Rock neutral N_1 sample, did not show sufficient signal to warrant further runs on the other samples.

2.4.11 Gas Chromatography/Mass Spectroscopy

Capillary-column gas chromatography/mass spectrometry (GC/MS) was used to study the organic materials extracted with ethyl acetate from the acidified permeates as well as the chromatographically separated acidic, neutral and basic organic fractions present in the permeates. In order to identify the major constituents of these samples/fractions, a variety of GC/MS techniques was employed, depending on the nature of the sample and the analysis objectives. Details on each of these techniques are given below. All GC/MS analyses were performed by the Chemistry Department of the University of Regina.

A. Direct Injection-GC/MS

The conventional procedure of directly injecting the sample into the GC sample port was followed for the ethyl acetate extracts (Battrum, Eyehill, Fosterton, Lone Rock and Meota), after these extracts (having a sample weight varying from 0.1 to 0.4 g) were redissolved in 1 mL of tetrahydrofuran (THF). (It was found later that the THF used contained a stabilizer [2,6-di-tert-butyl-4-methylphenol] to prevent the formation of peroxides.)

The gas chromatograph used for this study was a Hewlett Packard (HP) 5890, equipped with a capillary-column split injection port. The capillary column was a J&W Scientific, 35-m, fused-silica column (OV-351), having an inside diameter of 0.246 mm and a film thickness of 0.25 µm. This column, especially suited for the separation of polar organic constituents, was selected as the samples were anticipated to be predominantly polar in nature. Because of the small and varying amounts of sample provided, between three to five trial injections per sample were performed in order to optimize the operating conditions and obtain suitable chromatograms. The amount of injected sample was varied (from 2 to 6 µL) and/or the sensitivity of the detector adjusted (see below) so that smaller peaks in the chromatogram were sufficiently intense to rise above the computer threshold and could be detected by the program. The oven temperature was programmed to increase from 35°C to 240°C at a rate of 10°C/min, with a 10-min hold at 35°C and 240°C. The latter hold was to ensure that no more compounds were eluted and the detector current had returned to its normal base level. The injection port temperature was 250°C, while the temperature of the interface with the mass selective detector was 280°C.

The separated components were detected by an HP 5970A mass selective detector, operated by an HP 9825B computer. The GC/MS data were collected and analyzed using the Peakfinder program and stored on magnetic tape. The mass range scanned was from 15 (analytical pyrolysis) or 30 (all other analyses) to 300 AMU; other parameters were: threshold at 20 counts and EMV (electron multiplier voltage) varying from 1800-2400 V, depending on the concentration of the sample. In order to protect the detector, especially when analyzing aqueous solutions, the detector was turned off until the solvent peak was eluted.

B. Concentrator-GC/MS

A Chemical Data Systems GC concentrator Model 320 was used in combination with the above-described GC/MS equipment for the analysis of the aqueous and methanol solutions obtained from the chromatographic separation scheme. The instrument consists of two major components, the concentrator module, where the actual absorption/concentration process takes place, and the control module, which operates the concentrator module.

The concentrator methodology is based on sparging, that is the driving off of the organic compounds dissolved in a solvent by bubbling an inert gas (e.g. helium) through the sample solution, trapping these compounds on a packed tubular column (TENAX-GC) and then desorbing the concentrate into the GC by thermal pulsing. After the sample has been collected on the trap (before its introduction into the GC), excess solvent is removed using the DRY function of the concentrator module. The trap is then backflushed to vent using the trap carrier gas under specified conditions of time and temperature. Following the desorption of the sample and its introduction into the GC, the trap is reconditioned using the BAKE function.

For the acidic fractions, the capillary column used in the GC (OV-351) was the same column selected for the direct injection experiments. For the neutral and basic fractions a 50-m, cross-linked methyl silicone capillary column of 0.20 mm inside diameter and 0.50 μm film thickness was used.

Since the computer memory size and the data storage capacity on magnetic tape were limited and could only hold 90-100 mass spectra--not sufficient for some of the fractions--two injections were usually made for each fraction (at optimized conditions). For the first injection, the column temperature program was 35°C for 10 min, followed by a temperature increase at a rate of 20°C/min to a final temperature of 220°C, with a 10-min hold at that temperature. For the second injection the program was again 35°C for 10 min, followed by a temperature increase at a rate of 20°C/min to a temperature of 220°C with a 10-min hold, but then the temperature was further increased to a final temperature of 240°C with a 5-min hold. This hold was sufficient to ensure that no more compounds were eluted and the detector current had returned to its normal base level. The mass detector was always turned on 25 minutes from the time of injection.

Because the concentrations of the organics in the fractions were unknown, it was again necessary (as was the case for the direct injection runs) to inject each sample at least five times in order to optimize both the amount of sample injected and the detector sensitivity.

One of the major problems has been the damaging effect of water and methanol on the GC columns and mass detector. The acidic fractions contained compounds that had high boiling points (e.g. phenols and acids) and in order to extract them, the sparger temperature had to be very high (steam distillation). As a result, most of the water or methanol was evaporated and adsorbed in the trap along with the organic compounds. The only way to prevent these solvents from reaching the GC was to heat the trap to a high temperature or to increase the drying time. In both cases, all light ends in the samples would be vented as well. Chemical Data Systems was consulted, but it seemed that not much could be done as the concentrator was designed to extract only volatile compounds. In an attempt to detect as many components as possible, including those at the low and high ends of the boiling range, the sparger temperature was increased, while the drying time and temperature were decreased.

To minimize the extent of possible damage resulting from this approach, both acidic and basic fractions were concentrated to half their volume by rotary evaporation at room temperature. After concentration, the pH of the acidic fractions was adjusted to two using concentrated hydrochloric acid and the pH of the basic fractions to eight using concentrated sodium hydroxide.

Although useful qualitative results were obtained, the GC column did become damaged and had to be replaced. More seriously, although the mass detector was turned off whenever water or methanol was eluted, the sensitivity of the detector started to deteriorate rapidly, most probably the result of the presence of water and methanol in large quantities. In addition, the filament of the detector was damaged, most likely due to the same reason.

C. Analytical Pyrolysis-GC/MS

One of the main disadvantages of using the above-described conventional gas chromatography techniques for the separation of the compounds under investigation is that only the more volatile, lower-molecular-weight constituents reach the mass sensitive detector and, hence, can be detected. The heavier constituents, especially polar ones, tend to be retained by the column or get stuck at the injection port. Although raising the temperature may theoretically alleviate this problem, the port temperatures and upper column temperatures cited above were the highest possible working temperatures for this equipment and type of column. Even if higher operating temperatures were technically feasible, further temperature increases would still have to be limited because of the increasing probability of cracking of the heavier compounds. For these reasons another GC/MS technique has been employed that does provide chemical information, albeit indirectly, on all constituents in a sample. In this technique, called "analytical pyrolysis", the sample is subjected to a rapid temperature increase to 1400°C and the pyrolytic products so obtained are swept into the GC/MS apparatus for analysis.

A Chemical Data Systems Pyroprobe Model 122 was used to decompose the ethyl acetate extracts into volatile products, which were subsequently detected and identified by GC/MS. A THF solution of the material to be analyzed was prepared and 3.5 µL transferred to a platinum ribbon. The sample was spread as evenly as possible over the surface of the ribbon and the solvent was allowed to evaporate for 10-15 min. The probe was then inserted into the interface of the GC and after flushing with helium for 5 min the probe temperature was rapidly increased to 1400°C. The pyrolytic products were swept into the GC, fitted with a cryogenic valve, and passed through a 50-m, cross-linked methyl silicone capillary column of 0.20 mm inside diameter and 0.50 µm film thickness. The column temperature program was -80°C for one minute, followed by a temperature increase at a rate of 15°C/min to a final temperature of 220°C, with a 5-min hold at that temperature. The identities of all volatile products detected were verified by comparison with authentic compounds.

3. RESULTS AND DISCUSSION

3.1 WELLHEAD FLUID CHARACTERIZATION

Although outside the actual scope of the work, it was judged essential for this project to have information available on the characteristics of the wellhead fluids from which surfactants were to be extracted as well as of wellhead fluids from other wells in the project area. Data on the latter permit a comparison of the sampled wells with the surrounding field and an assessment as to how far these sampled wells deviated from the norm. Hence, data on the physical and chemical properties of the oil and water phases produced by the study wells are provided in Tables 3 and 4, as well as the ranges and the averages of the corresponding properties for all the wells regularly monitored by SRC in the respective areas (the number of wells on which the averages were based is given in backets). No field-wide data were available for the Fosterton N.W. project, as this pilot is not monitored by SRC. This is also the reason that only limited wellhead fluid data are shown for the study well itself.

Keeping in mind the criteria used in the selection of the study wells, some interesting observations can be made from the data in Tables 3 and 4. With respect to oil characteristics, the Battrum, Lone Rock and Meota samples were typical for their respective fields, hardly differing from the norm. It should be noted, however, that the collected Battrum emulsion sample did have the highest water content (60% v/v) of all wells in the area. The characteristics of the Eyehill oil sample were slightly different from the rest of the wells in the pilot, as is exemplified by the elevated levels of the acid numbers, the slightly lower API gravity and the increased asphaltene content. Elevated acid numbers have been interpreted to indicate low-temperature oxidation of the oil.[83-86] Surprisingly, the water content of the Eyehill sample (10%) was the lowest encountered in the pilot. Although no field data were available on the Fosterton pilot, oil and water characteristics may be assumed to be comparable to the data from

Table 3. Chemical and Physical Properties of Oil Produced by Study Wells and Surrounding Field

	W/O Emulsion	API Gravity	Viscosity @ 40°C (mPa•s)	Sulphur (wt %)	Asphaltenes (wt %)	Acid Number (mg KOH/g)			
	BS&W (Vol %)					Very Strong	Strong	Weak	Total
Battrum (10/86)									
7-26	60	16.1	161	3.43	12.9	N.D.	0.23	0.17	0.40
Range	3-60	15.5-17.8	97-187	3.31-3.54	10.9-14.7	N.D.	0.17-0.50	0.13-0.70	0.31-1.20
Average (11)	30	16.5	147	3.43	12.6	N.D.	0.26	0.23	0.49
Eyehill (2/87)									
16-16	10	13.1	788	3.02	12.4	0.59	1.67	0.54	2.80
Range	10-50	12.6-20.6	26-1054	2.53-3.16	8.1-12.7	0-0.59	0.83-1.67	0.08-0.54	1.18-2.80
Average (18)	25	13.5	769	3.04	10.9	0.16	1.19	0.26	1.61
Fosterton (5/87)									
1B-15	76	12.6	762	3.44	-	-	-	-	-
Lone Rock (9/87)									
3D4*	40	17.7	162	3.28	11.0	N.D.	0.58	0.31	0.90
Range	9-74	14.8-18.2	133-579	3.14-3.57	10.9-12.3	0-0.09	0.51-0.64	0.30-0.47	0.87-1.11
Average (6)	40	16.9	283	3.36	11.4	0.02	0.59	0.34	0.94
Meota (7/86)									
4D8	17	11.3	4070	3.62	13.9	0.09	1.03	0.34	1.46
Range	8-42	10.9-11.8	2960-6080	3.56-3.69	13.3-14.8	0.04-0.17	1.02-1.09	0.17-0.44	1.33-1.59
Average (7)	22	11.3	4384	3.63	14.0	0.09	1.06	0.29	1.45

N.D.: Not Detected.

* Data used from September 1987 since the wellhead sample collected for this study in September 1986 did not contain sufficient oil for analysis.

Table 4. Chemical and Physical Properties of Water Produced by Study Wells and Surrounding Field

	pH	Total Alkalinity (as $CaCO_3$ equiv., mg/L)	Conductivity (mS/cm)	K (mg/L)	Na (g/L)	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)	Cl (g/L)	SO_4 (mg/L)	Carboxylic Acids				Phenols (mg/L)
											C_2 (mg/L)	C_3 (mg/L)	C_4's (mg/L)	C_5's (mg/L)	
Battrum (10/86)															
7-26	6.3	2274	12.8	26.2	3.2	444	65	15.1	3.8	2075	1287	27.9	5.7	6.2	0.31*
Range	6.2-8.6	1043-3998	7.8-17.5	8.0-44.6	2.0-3.5	15-1797	5-530	0-299	0.8-3.9	5-2750	0-1897	0-71.3	0-29.0	0-17.2	0-8.23*
Average (13)	6.9	2655	11.2	18.0	2.7	382	148	57.7	2.7	1337	582	25.0	7.6	5.1	0.96*
Eyehill (2/87)															
16-16	3.3	N.D.	35.2	501	6.8	355	442	3230	13.4	5400	2224	87.2	40.2	23.8	4.27*
Range	3.3-7.9	0-1787	26.4-78.5	177-601	6.1-29.6	355-1680	221-645	0-3230	10.0-36.8	22-5400	0-2224	0-87.2	0-40.2	0-23.8	0-28.6*
Average (18)	6.4	1121	65.4	487	19.4	1130	538	196	30.2	615	175	6.9	3.3	2.1	3.26*
(16-16, after mixing)†				(28.6)	(0.39)	(20.2)	(25.2)	(184)	(0.76)						(0.24)
Fosterton (5/87)															
1B-15	3.0	-	10.8	30.5	2.4	56.9	56.1	550	3.7	2000	-	-	-	-	-
(1B-15, after mixing)†				(7.9)	(0.62)	(14.8)	(14.6)	(143)	(0.96)						
Lone Rock (9/86)															
3D4	7.7	80	3.0	35	0.52	1	1	0.1	0.66	140	N.D.	N.D.	N.D.	N.D.	0.08
Range	5.9-7.7	80-576	3.0-46.4	35-198	0.52-11.4	1-772	1-409	0.1-8.4	0.66-16.8	30-256					0.08-6.56
Average (12)	6.4	248	13.1	92	2.9	124	75	1.9	4.3	138	N.D.	N.D.	N.D.	N.D.	2.07
Meota (7/86)															
4D8	5.1	250	3.9	65	0.84	N.D.	N.D.	N.D.	1.1	55	2	N.D.	N.D.	N.D.	1.25
Range	5.1-7.3	190-1071	3.9-60.0	59-438	0.84-17.7	0-421	0-366	0-0.04	1.1-25.7	22-625	0-11	0-4.0	0-2.0		0.15-6.08
Average (11)	6.5	537	25.0	179	6.1	160	119	0	9.1	179	4	1.0	0.2	N.D.	2.54

N.D.: not detected
*Wells sampled 9/87.
†See Section 3.2.

the nearby Battrum field. The Fosterton sample included in this study had a very high water content (76%) and was difficult to break.

The water characteristics of the sampled wells showed more dramatic differences compared to other wells in the respective fields. As can be concluded from the greatly reduced dissolved solids contents of the produced water from the sampled Lone Rock and Meota steamflood wells, mixing with substantial amounts of fresh water (presumably arising from the condensation of the injected steam) must have occurred before or during the production of these wells. Consequently, the possibility is raised that this mixing phenomenon may be correlated with the formation of the observed o/w emulsions in these cases.

The fireflood wells did not exhibit such a unified behaviour in their produced water. The characteristics of the water produced by the Battrum well selected for sampling were close to average as far as most dissolved solids were concerned, although there were definite effects of the fireflood, i.e. a somewhat lower pH and increased levels of sulphate and acetic acid.[85,86] The sampled Eyehill well dramatically demonstrates the fireflood effects on produced water, when, as is speculated here, the firefront approaches a well. As a result of combustion and low-temperature oxidation processes the pH dropped to around three, while the levels of sulphate and carboxylic acids (C_2 through C_8) rose steeply. As a result of dilution with fresh water from the steam plateau or the combustion itself, the concentration of most dissolved solids was lower, with the exception of iron which also jumped steeply because of increased corrosion of the well. The available data on the Fosterton produced water showed both similarities with the Eyehill sample (low pH and elevated iron level) and with the Battrum sample (similar conductivity and cation concentrations and increased sulphate level).

The following summarizes the above analysis of the oil and water characteristics of the wells sampled for this project:

- The selection of the wells sampled in the three fireflood projects (Battrum, Eyehill and Fosterton) was based on the propensity of these wells to produce extremely stable w/o emulsions. Most other wells in these projects produced emulsions that were easier to treat.

- The sampled Battrum oil did not appear to be effected by the fireflood and was similar to the rest of the field. The Eyehill oil had somewhat elevated acid numbers.

- The sampled Battrum produced water started to show signs of fireflood effects, while the Eyehill water (and the Fosterton water to some extent) exhibited severe effects (low pH, very high levels of sulphate, carboxylic acids and iron).

- Wells sampled in the Lone Rock and Meota steamflood projects were selected for their propensity to produce stable o/w emulsions (in the water phase). Only a few wells exhibited this phenomenon.

- The sampled Lone Rock and Meota oils did not differ in any way from their field averages.

- The sampled Lone Rock and Meota produced waters were significantly diluted with fresh water, presumably by the mixing in of condensed steam.

3.2 CHARACTERIZATION OF RAW PERMEATES

Following the sample preparation and ultrafiltration procedures outlined in Sections 2.1 and 2.2, respectively, permeates were obtained from the water phases associated with seven wellhead emulsions, taken from the five study wells identified in Section 2.1.1. As described in Section 2.1.2 three separate samples were obtained from Lone Rock well 3D4 at the same time. One sample was subjected to ultrafiltration one day after its arrival in the laboratory, while the other two samples were allowed to age one week and one month, respectively, before they underwent ultrafiltration.

The seven raw permeates were submitted to various chemical and physical analyses, the results of which are given in Table 5. These analyses will be discussed individually and, in order to examine the effects of membrane permeation, compared with the results (Table 4) of the analyses on the respective produced waters (i.e. permeation feed waters). To facilitate this comparison a correction had to be applied to the Eyehill and Fosterton feed water data. Although in the Eyehill and Fosterton cases just enough free water was produced to allow for regular analysis, mixing of both emulsions with added deionized water was required to create sufficient water for ultrafiltration. Although this feed water was not reanalyzed, an estimate of the various ionic concentrations (shown in brackets in Table 4) was made by correcting for dilution. This correction was based on the assumption that the dissolved species were originally only contained in the water phase emulsified in the oil. It was also assumed that the concentrations of the species dissolved in the emulsified water would be the same as those in the small quantity of produced water analyzed.

3.2.1 pH

Comparison of the pH levels before and after permeation reveals a tendency for the pH to increase upon permeation. This is most noticeable in the Meota case. Dissolved gases (CO_2) were likely responsible for the

Table 5. Chemical and Physical Properties of Permeates

	pH	Alkalinity	Acidity	TOC (mg/L)	Conductivity (mS/cm)	K (mg/L)	Na (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)	Cl (mg/L)	Si (mg/L)	Phenols (mg/L)	IFT (dy/cm)
		(as $CaCO_3$ equiv., mg/L)												
Battrum	6.9	2044 @ pH=4.1	34.8 @ pH=8.0	1120	14.6	23.5	3060	372	62.3	14.6	3807	3.4	10.4	3.8
Eyehill	3.4	NE	42.7 @ pH=6.4	200	0.7	7.3	57.2	32.1	17.2	34.9	42.5	0.6	14.3	25.4
Fosterton	3.7	NE	421 @ pH=5.9	952	3.2	12.3	529	15.7	17.6	458	601.7	6.2	0.83	20.1
Lone Rock														
Unaged	7.8	56.9 @ pH=4.7	NE	38	2.0	33.4	473	0.48	0.29	0.3	535	39	4.74	10.5
1 Week	7.6	55.6 @ pH=4.7	NE	31		34.0	431	0.66	0.34	<0.2	524	81	4.78	
1 Month	7.5	63.9 @ pH=4.7	NE	38		32.0	462	0.47	0.89	0.05	625	71	7.35	
Meota	9.0	20.6 @ pH=8.5 213 @ pH=3.9	NE	76	3.5	63.0	668	<0.06	<0.01	0.2	920	25	7.44	7.1

NE : No endpoint

IFT: Measured against neutral oil (see text).

lower pH of the (fresher) produced water.

3.2.2 Acid/Base Titrations

Titrations with acid and base were performed to determine the alkalinity and acidity of the permeates. Alkalinity is a measure of the buffering capacity to neutralize acid, while acidity measures the buffering capacity to neutralize base. In the titration with acid, inflection points in the titration curves were observed at pH 8.5 (Meota) and between pH 3.9-4.7 (Battrum, Lone Rock, Meota). The former inflection point indicates the presence of carbonates, while the latter is indicative of the presence of bicarbonates and alkaline materials, including organic bases and ionized salts or organic acids. Not surprisingly, the already highly acidic Eyehill and Fosterton samples did not exhibit any inflection points when the pH was further reduced. The total alkalinities of the permeates measured at pH 3.9-4.7 were only slightly lower than the total alkalinities of the corresponding produced waters (Table 4), which were determined by titration with HCl using methyl orange (endpoint at pH 4.0-4.5) as indicator.

The Battrum permeate acidity is relatively low at the pH 8 inflection point. The increased acidities at lower pH values for the Eyehill and Fosterton permeates are most likely due to the higher iron content. Iron interferes with the base titration as it forms insoluble $Fe(OH)_3$; it would have to be removed to obtain the acidities of any organic compounds present. Calcium and magnesium may also interfere as they tend to form carbonate/bicarbonate buffers.

3.2.3 Total Organic Carbon

Inorganic carbon (IC) and total organic carbon (TOC) contents were determined for all permeates and most feed waters (Table 6). TOC levels in the fireflood waters (Battrum, Eyehill and Fosterton) were discussed in detail in Section 2.1.2. No TOC analyses were performed on the steamflood produced waters (Lone Rock, Meota) collected early in the study. However,

Table 6. Organic and Inorganic Carbon Content of Water Samples Before and After Permeation†

	Produced Water/ Free Water After Mixing (mg/L)			Permeate (mg/L)		
	TC	IC	TOC	TC	IC	TOC
Battrum	1270	160	1110	1250	132	1120
Eyehill	152	2	150	208	8	200
Fosterton	1146	13	1133	952	<1	952
Lone Rock						
Unaged	-	-	-	45	7	38
1 Week	-	-	-	38	7	31
1 Month	-	-	-	48	10	38
Unaged*	110	19	91	140	30	110
Meota	-	-	-	110	34	76

† TC = Total Carbon; IC = Inorganic Carbon; TOC = Total Organic Carbon.

* Second Lone Rock 3D4 sample, obtained on January 3, 1987.

the TOC level in a second, unaged, Lone Rock produced water sample (collected because of the low yield of extracted organic materials from the first sample) was an order of magnitude lower than the Battrum and Fosterton TOC levels.

Comparison of TOC levels before and after permeation does not reveal major changes. Only the TOC level in the Eyehill permeate appears to have significantly increased. Since it was found that phenols tended to concentrate in the permeate (see Section 3.2.5 below) and that the Eyehill permeate showed one of the highest levels of phenols (see results of characterization in Sections 3.5 and 3.7), this increase in TOC could be explained.

There is a clear parallel between the permeate TOC values and the corresponding total alkalinities (Table 5) discussed in Section 3.2.2 (Battrum, Lone Rock and Meota), having taken into account the contributions of the inorganic carbon (IC) compounds (carbonates/bicarbonates) to the total alkalinities. This agreement suggests that the dissolved organic material consists primarily of salts of organic acids and, possibly, organic bases.

3.2.4 Dissolved Salts

Permeation through the Nylon-66 0.2 µm membrane did not affect the K^+, Na^+, Ca^{2+}, Mg^{2+}, Fe^{2+} and Cl^- concentrations to any significant degree. In the directly comparable cases (Battrum, Lone Rock and Meota), the permeate concentrations of most of these ions were only slightly lower than the corresponding ones in the feed water. Because of their generally higher levels, this drop is most noticeable in the sodium and chloride concentrations (down 10-20%). The Fosterton permeate data follow the same trend, when compared with the apparently slightly underestimated feed water data. A much increased iron concentration in the Fosterton permeate is observed, likely due to corrosion of the sample drum. Comparison of the Eyehill permeate and estimated feed water data provides a challenge. If the dilution correction was correct (the approximate similarity of the K^+, Ca^{2+}, and

Mg^{2+} levels would support this), concentrations of Cl^-, Na^+ and Fe^{2+} would have decreased by factors of 18, 7 and 5, respectively. Such reductions were not observed in the other four permeates.

The conductivity data shown in Tables 4 and 5 may be used as indicators of TDS (total dissolved solids) analyses; both properties are measures of the dissolved salt concentrations.

3.2.5 Phenols

Comparison of the phenol levels in the feed waters and the permeates is complicated by the fact that a slightly different method was employed for the analysis of phenols in produced water, and that data from other sampling dates (Battrum, Eyehill) were included. The consistently higher phenol levels in the permeates do appear to indicate, however, that permeation had a concentrating effect.

Comparison of the phenol levels in the three Lone Rock permeates (unaged, one week and one month) shows the one-month level to be 50% higher. This increase and the slightly higher alkalinity of the 1-month permeate are the only changes observed when comparing the three permeates. Since the measured phenol content usually tends to decrease on aging (unless a preserving agent is added), the increase shown here is likely due to experimental and random errors.

3.2.6 Interfacial Tension

Interfacial tension (IFT) measurements were included in this study to provide a means of assessing the effect on interfacial tension by the surface active materials (surfactants) expected to be isolated. A lowering of the interfacial tension between the dispersed phase and the continuous phase is traditionally believed to be conducive to emulsion stability. Therefore, determining the interfacial tension lowering capability of the isolated surfactants could provide an avenue to pinpoint the "bad actors" causing stable emulsions. However, as discussed in the literature review (Section 1.3) and repeated by recent publications,[87-88] things may not be so simple. Although Rosano[88] stated that "a sufficiently low positive value of the interfacial tension is always better for emulsion formation," emulsion stability is not solely dependent on the value of the interfacial tension, but also on the structure of the interfacial film surrounding the individual droplets.[87] In addition, many other parameters are known to affect the interfacial tension, e.g. salinity, nature of crude oil or solvent used, temperature, equilibrating time, etc. Thus interpretation of the interfacial tension data below in terms of emulsion stability remains a controversial topic and should be carried out with caution.

Originally, interfacial tension measurements were planned on both the raw permeates and the isolated organic materials, but the type of systems to be measured (i.e. choice of continuous and dispersed phases) was not further defined. Interfacial tension measurements on systems similar to the actual steamflood and fireflood emulsions would obviously be the most desirable. For the various permeates, this would imply using as the reference oil the respective wellhead oils associated with these permeates. However, the reference oil must be water- and surfactant-free, and dehydrating the very tight fireflood emulsions sampled for this project without the use of demulsification chemicals proved to be impossible. It was, therefore, decided to use as the reference oil a readily available neutral oil (a light gas oil obtained from the Co-op refinery in Regina), against which all permeates would be compared. It should be noted, however, that because of the different chemical composition of this oil as compared to the various wellhead oils, interfacial tension effects found for the permeate/neutral oil systems may not apply to the permeate/wellhead oil systems.

Interfacial tension is very sensitive to the presence of any dissolved matter. Since the permeates contained varying amounts of dissolved inorganic salts in addition to dissolved organic material, any measured effect on the interfacial tension would be a combination of effects by these two compound groups. In an attempt to separate and quantify the contribution by dissolved salts, two brine solutions with a low and a high total dissolved solids (TDS) content were prepared. These solutions reflected the typical salt composition and concentration of a Battrum and an Eyehill brine, respectively. The results of the interfacial tension measurements of the neutral oil in deionized water and in the two synthetic brines are given in Table 7. Also included for comparison are the interfacial tensions of the neutral oil and a Lone Rock oil (dehydrated without chemicals) in an aqueous solution of an active surfactant (SRC-K1). It can be seen that a high salt content alone can produce a considerable lowering of the interfacial tension, but the greatest reduction was achieved with the surfactant. Turning now to the neutral oil/permeate results and using the conductivity as a measure of the TDS content, it is obvious that the very significant interfacial tension reduction by the Battrum permeate could not have been caused by the dissolved salts alone and must, therefore, be largely due to dissolved organic materials with surfactant properties. The high TOC level of the Battrum permeate would be consistent with this conclusion. Surprisingly, the other two fireflood permeates did neither affect the interfacial tension (Fosterton) nor adversely affect it (Eyehill). Since the Fosterton TOC level was very similar to that of Battrum, the conclusion here must be that the organic substances in the Fosterton permeate did not exhibit measurable interfacial activities.

Both steamflood permeates showed considerable interfacial activity, especially considering their low TOC contents.

The effect of the oil type on interfacial tension was briefly examined by comparing the neutral oil/Lone Rock permeate interfacial tension with the result from a Lone Rock oil/Lone Rock permeate system. Whether the observed higher interfacial tension of the latter (similar to that of the neutral oil/deionized water system) indicates that the Lone Rock permeate is not effective here or that a Lone Rock oil/deionized water system would have a still higher interfacial tension cannot be answered without further experiments.

Table 7. Interfacial Tension Measurements.

Oil/Water Systems		Conductivity (mS/cm)	TOC (mg/L)	IFT* (dy/cm)
Oil Phase	Aqueous Phase			
Neutral Oil	Deionized water			20.3
Neutral Oil	5400 ppm TDS in deionized water	10.4		15.2
Neutral Oil	58,550 ppm TDS in deionized water	76.5		8.1
Neutral Oil	0.01% SRC-K1 in deionized water			2.7
Lone Rock 2A5	0.01% SRC-K1 in deionized water			1.9
Neutral Oil	Battrum permeate	14.4	1120	3.8
Neutral Oil	Eyehill permeate	0.72	200	25.4
Neutral Oil	Fosterton permeate	3.2	952	20.1
Neutral Oil	Lone Rock permeate (unaged)	2.0	38	10.5
Neutral Oil	Meota permeate	3.5	76	7.1
Lone Rock 2A5	Lone Rock permeate (unaged)	2.0	38	20.2

* Measured at 20°C.

Interfacial tension measurements were originally also planned on the isolated organic materials. By dissolving these substances in pure water a direct and more quantitative approach for assessing the interfacial activities of these organic materials would be achieved, without the interference of other dissolved substances. Unexpectedly, however, the organic materials could not be redissolved and this characterization step had to be abandoned. The failure of the ethyl acetate extracts to redissolve in water was blamed in part on the loss of low-molecular weight compounds (light ends) during sample workup.

3.3 CHARACTERIZATION OF DRIED PERMEATES

The originally proposed separation and analysis schedule called for acidification of the raw permeates to pH 2. This was expected to cause precipitates (presumably insoluble organic acids and phenols), which were to be characterized by a wide variety of analytical methods.

Because it proved impractical or impossible to generate sufficient quantities of acid precipitates for the analyses originally envisaged, the separation and characterization schedule was revised, with more importance placed on the characterization of the ethyl acetate extracts and the chromatographically separated fractions.

In order to obtain a preliminary examination of the organic materials present in the raw permeates before these extraction and separation steps, it was also decided to characterize (by elemental analysis and infrared spectroscopy) the dried residues obtained by removing the water from the raw permeates through freeze-drying and rota-evaporation.

Although quantitative recovery of these residues and other products in this study (i.e. the ethyl acetate extracts and the dried residues from the water phases after extraction) was not emphasized--the main problem encountered was the complete removal of the solvents (water, ethyl ecetate)--recovery yield data have been obtained for most products (Table 8). The data in the first column of this table are the yields of the raw permeate residues. As expected, these yields closely parallel the raw permeate conductivity data of Table 5 (representing the amount of total dissolved solids).

3.3.1 Elemental Analysis

The elemental analyses of the residues obtained after drying the raw permeates are given in Table 9. No particular significance can be attached

Table 8. Product Yields of Dissolved Organic and Inorganic Materials

	Dried Residue From Raw Permeate (mg/L)	Ethyl Acetate Extract From Acidified Permeate (mg/L)	Dried Residue From Aqueous Phase After Extraction (mg/L)
Battrum	11085	621	7421
Eyehill	606	47	741
Fosterton	1664	368	3292
Lone Rock			
Unaged	1130	+	+
1 Week	1140	74	958
1 Month	1250	124	+
Unaged*	N/A	141	+
Meota	1615	+	+

+ Samples incompletely dried.

* Second sample, obtained on January 3, 1987.

Table 9. Elemental Analysis of Dried Permeates

	Elemental Analysis (Wt %)				C/H Ratio
	C	H	N	S	
Battrum	7.30	1.05	0.01	<0.02	0.58
Eyehill	17.0	3.0	0.03	4.9	0.47
Fosterton	12.0	2.0	0.09	1.23	0.50
Lone Rock					
Unaged	1.58	0.34	0.06	0.56	0.39
1 Week	1.37	0.24	0.02	0.87	0.48
1 Month	1.41	0.29	0.02	<0.02	0.41
Meota	1.84	0.35	0.02	<0.02	0.44

to the carbon, hydrogen, nitrogen and sulfur contents in an absolute sense, as these are determined by the ratios of the organic and inorganic fractions in the residues, and hence in the permeates. It is obvious, nevertheless, that the nitrogen content in all samples was very low, thus reducing the possibility that basic compounds could constitute a significant portion of the organic materials. The sulfur contents generally appeared to be fairly low as well. The high sulfur content of the Eyehill and Fosterton residues was almost certainly due to the high sulfate levels in the permeates. It is unclear why the Battrum residue did not exhibit a similar or even higher sulfate content.

The carbon-to-hydrogen (C/H) ratios may provide more useful information on the organic components, if interference from water and carbonates can be excluded. Although this may not be the case for the Battrum sample with its higher inorganic carbon content (refer to Table 6), there does appear to be a trend, with the steamflood samples having a somewhat lower C/H ratio and, therefore, being more aliphatic than the fireflood samples.

3.3.2 Infrared Analysis

Because of the many compounds anticipated to be present in the various organic fractions isolated in this and following separation steps, it was not feasible to analyze every infrared absorption band in terms of the vibrational modes in each compound. The emphasis of the infrared analyses in this study was, therefore, on the determination of the classes of compounds thought to be present in each sample. Comparisons were made based on the well origins of each sample, and the question was addressed whether any differences arose from the samples produced by steamflood as opposed to fireflood techniques. All infrared spectra discussed in this chapter are shown in Appendix B.

The infrared spectral data on the dried residues obtained from the raw permeates are listed in Table 10.

Table 10. Infrared Absorption Data of Dried Permeates

Wavenumber (cm^{-1})						Vibrational Mode
Firefloods			Steamfloods		Blank KCl Pellet With Water Added	
Battrum	Eyehill	Fosterton	Lone Rock	Meota		
3400	3450,3200	3400	3400	3480	3400	- H_2O; carboxylic acid O-H stretch; phenol or alcohol O-H stretch
3000	3000,2960 2860	2940 sh	3000	2940 sh		- C-H stretch
2500						- Thio-compounds S-H stretch
	2360,2340					- Unassigned
					1670,1640	- H_2O, olefinic C=C stretch
1570	1570	1560	1570	1570		- Carboxylic acid anion C-O stretch
1420	1430	1420	1420	1440		- Carboxylic acid anion CO_2 symmetric stretch; carbonate ions CO asymmetric stretch; alkyl CH bending; aromatic skeletal vibrations; carboxylic acid COH in-plane bending; C-H bending
					1160	- H_2O
1130	1100	1130	1095	1060		- Phenol or alcohol C-O stretch; aromatic ring C-H bending
930	940 sh					- Carboxylic acid O-H out-of-plane bending
870	875					- Carbonate ion CO_3 deformation out-of-plane
	825					- Unassigned
650	670	660				- C-H bending, carbonate ion CO_3 deformation in-plane
					640	- H_2O
620	600	615	610	630,600		- Unassigned
	540	530 sh				- Unassigned
470	470	470 sh	470	480	470	- H_2O

sh = shoulder

a) Presence of Solvent

Water is known to be highly absorbing in the infrared region, with the following frequency ranges absorbing at least 75% of the incident energy in a 0.01-mm sample: 3650-2930 cm^{-1}, 1750-1580 cm^{-1}, and below 930 cm^{-1}.[89] Absorption bands for a blank (KCl pellet with water added) are listed in Table 10. Although the presence of water in the dried residues could be indicated by the broad O-H stretching band at 3480-3400 cm^{-1}, other water bands showing up in the blank spectrum are absent in the spectra of the residues and, therefore, little water is thought to be present in these samples.

b) Functional Groups

The IR spectra of the five samples are very similar, with some additional weak bands being present in the more detailed Eyehill and Battrum spectra. The broadness of the bands confirms the theory that many compounds are present.

As mentioned above, the broad band centered at 3480-3400 cm^{-1} could have some contribution from residual water, but owes most of the absorption to the O-H stretch of carboxylic acids, alcohols and phenols. Spectra of carboxylic acids manifest a strong C=O stretching absorption band around 1700 cm^{-1}. Although no actual "peaks" occur at 1700 cm^{-1}, this does not mean that no carboxylic acids are present. Considerable absorption occurs at 1700 cm^{-1}, buried in the band with maximum absorbance at 1570-1550 cm^{-1}.

Other bands due to phenols and/or alcohols include the broad, strong C-O stretching vibration in the 1130-1060 cm^{-1} range. A weaker band would be expected in the 1420-1330 cm^{-1} range; it could be obscured by the 1440-1420 cm^{-1} band.

The presence of carboxylic acid anion should be mentioned as a possibility, since the raw permeates had not been acidified. The C=O stretch, located at 1700 cm^{-1} for carboxylic acids, shifts to a much lower frequency (1650-1550 cm^{-1}) in carboxylic acids anions, since resonance makes the two oxygen atoms equivalent and thus each C-O bond intermediate between double and single bond strength. This band is present in all samples, but it is broader than expected for this one vibrational mode. Likely, this band receives an absorbance contribution from the carboxylic acid anion C-O stretch, as well as from other functional group vibrations. Carbonate ions could also be present. The strong absorbance in the 1440-1420 cm^{-1} region, present in the spectra of all samples, could be partly due to the CO asymmetric stretch of carbonate ions. Other bands due to carbonate ions could be the 875-970 cm^{-1} band, visible in the more detailed spectra of Battrum and Eyehill, and a 720-680 cm^{-1} band, although the latter is said to be unreliable.[89]

The spectrum of the Battrum sample shows a weak band at 2510 cm^{-1}. Although weak, the location of this band is distinctive and indicative of the S-H stretch in thio-compounds.

There are likely many functional groups present in these samples whose vibrational modes give rise to absorbance bands less intense and in less distinctive locations. These bands are obscured by the larger bands. For example, it is extremely difficult to determine if N-H groups are present. N-H vibrational modes for amides and amines absorb in the following regions: 3500-3400 cm^{-1}, 1655-1620 cm^{-1}, 1570-1515 cm^{-1}, 1400 cm^{-1}, 800-666 cm^{-1}, 1650-1580 cm^{-1} and 1342-1266 cm^{-1}. All of these regions show absorption, but the band maxima in the five spectra do not correspond with the set of N-H bands expected. Compounds containing NH groups may occur in too low a concentration to be detectable.

Of course, the ubiquitous bands due to various alkyl, aromatic and olefinic groups are weakly present, and some vibrational modes thought to be visible are listed in Table 10.

c) Spectral Differences Between Individual Samples

Although some intensity differences in bands occurred due to pellet thickness differences, the infrared spectra of the three Lone Rock samples aged one day, one week and one month, respectively, were virtually the same. This was true for the products examined in this section (dried permeates) as well as for the precipitates from acidification and the ethyl acetate extracts, both of which will be discussed in the following sections. Consequently it was concluded that as far as infrared analysis was concerned no effects of sample aging were detectable. (Likewise, no differences had been detected in the permeation behaviour of the three variously-aged Lone Rock emulsions.) For these reasons, most other Lone rock analyses referred to in this chapter were performed only on material obtained from fresh (aged one day) emulsion. Similarly, unless specified otherwise, discussions in this chapter will pertain to fresh-emulsion-derived products and analyses.

Overall, the spectra of the five samples are remarkably similar, with only the intensity ratios of some bands varying somewhat from spectrum to spectrum. The spectra arising from the two steamflood samples (Lone Rock and Meota) are essentially identical. More variation and differences exist in the spectra of three fireflood samples (Battrum, Eyehill and Fosterton). The appearance of the many weak peaks in the Eyehill spectrum and, to a lesser extent the Battrum spectrum, are however attributed to differences in concentration or pellet thickness. The presence of the S-H band (2510 cm^{-1}) in the Battrum spectrum may mean a higher concentration of thio-compounds or merely a lower ratio of inorganic salt to thio-compounds than in other samples.

As far as differences between the spectra from the steamflood and fireflood samples are concerned, one evident trend was the shift of the 1095-1060 cm^{-1} band in the steamflood-derived samples to the 1130-1100 cm^{-1} region in the fireflood samples. This absorbance, attributed to the C-O stretching vibration for alcohols and phenols, is known to be sensitive to the skeletal structure of the alcohol/phenol molecule, with absorbance at higher frequencies thought to occur in more aromatic structures.[90] Thus, the Battrum, Eyehill and Fosterton samples may have contained a higher ratio of phenols to saturated alcohols than the two steamflood-derived samples.

3.4 CHARACTERIZATION OF ACID PRECIPITATES

As referred to in Section 3.3, the acid precipitates originally anticipated were only observed in the Lone Rock and Meota steamflood cases. Despite various attempts to increase the yields (e.g. by concentrating the permeates), the quantities of precipitate recovered--even from large volumes of permeate--were so small that only infrared analyses could be performed. No further attempts were made to produce and recover acid precipitates from the three fireflood permeates.

3.4.1 Infrared Analysis

The infrared spectra of the acid precipitates from the Lone Rock and Meota permeates were almost identical, as can be seen from the tabulation of absorption bands in Table 11. It is believed that water was present in both the Lone Rock and Meota samples. Absorption bands at 3390-3360 cm^{-1}, 1640 cm^{-1}, 1100 cm^{-1}, 640-550 cm^{-1} and 475-470 cm^{-1} matched the location and shape of similar bands in the blank spectrum (KCl pellet with water added).

The remaining bands were similar to those attributed to carboxylic acids in the dried permeates, ethyl acetate extracts and chromatographic fractions. Detailed analyses of these bands can be found in the corresponding sections below.

Since phenols exhibit absorption bands at two of the same frequencies as the blank (3390-3360 cm^{-1} and 1100 cm^{-1}), the possibility that phenols were present in the acid precipitates could neither be confirmed nor eliminated.

Table 11. Infrared Absorption Data of Acid Precipitates

Wave Number (cm^{-1})			Vibrational Mode
Steamfloods		Blank KCl Pellet With Water Added	
Lone Rock	Meota		
3390	3360	3400	- Carboxylic acid O-H stretch; H_2O
2960,2925 2870	2960,2880		- C-H Stretch
1700	1700		- Carboxylic acid C=O stretch
1640	1640	1670,1640	- H_2O
1450	1440		- Carboxylic acid COH in-plane bending
1220 sh	1280,1210		- Carboxylic acid dimer CO stretch
1100	1100	1160	- H_2O; phenols C-O stretch
955			- Carboxylic acid OH out-of-plane bending
800	840		- Unassigned
550	640	640	- H_2O
470	475	470	- H_2O

sh = shoulder

3.5 CHARACTERIZATION OF ETHYL ACETATE EXTRACTS

Organic materials thought to consist of emulsion-stabilizing surfactants were recovered by extracting the acidified permeates with ethyl acetate and subsequently removing the solvent by rota-evaporation, followed by further drying in a vacuum autoclave. Table 8 shows the yields of most of these organic products. Although the product yields appear to generally follow the variations of the TOC levels in the raw permeates (Table 5), there are differences in the relative magnitudes of some yields. In particular, the Battrum and Lone Rock yields seem too high in comparison to the corresponding TOC values. Part of this disagreement may be due to incomplete solvent removal (the NMR analyses in Section 3.5.6 revealed that both the Lone Rock and Fosterton samples could contain around ten mole percent ethyl acetate). However, since the Battrum sample contained only a trace of ethyl acetate and the Eyehill sample none, the apparent high Battrum yield must be due to another reason. Indeed, as will be discussed below, anomalies in the elemental analysis of the Battrum product suggest that inorganic salts were present in the isolated material and hence contributed to the weight of the recovered product.

The isolated organic materials were subjected to a range of characterization techniques, including elemental analysis, molecular weight determination, acid number determination (base titration), thermal gravimetric analysis, infrared analysis, ^{13}C NMR spectroscopic analysis and GC/MS analysis. The results of these analyses will be discussed in the following sections.

3.5.1 Elemental Analysis

The elemental analyses of the ethyl acetate extracts are shown in Table 12. While values for the carbon and hydrogen contents of the Eyehill, Fosterton and Lone Rock samples are found in a narrow range, the

Table 12. Chemical Analyses of Ethyl Acetate Extracts

	Elemental Analysis (Wt %)					C/H Ratio	Mol Weight (g/mol)	Acid Number (mg KOH/g)			
	C	H	N	S	100-C-H			Very Strong	Strong	Weak	Total
Battrum	24.2	2.41	I.S.	0.03	73.4	0.84	242.0	N.D.	580.1	N.D.	580.1
Eyehill	63.9	7.6	I.S.	I.S.	28.5	0.70	125.0	N.D.	230.0	N.D.	230.0
Fosterton	61.8	6.2	0.08	I.S.	32.0	0.83	199.0	N.D.	288.2	N.D.	288.2
Lone Rock (Unaged)	60.2	6.74	0.22	I.S.	33.1	0.74	184.0	N.D.	198.8	54.9	253.7
Meota	I.S.	I.S.	I.S.	I.S.	-	-	I.S.	I.S.	I.S.	I.S.	I.S.

I.S.: Insufficient Sample. N.D.: Not Detected.

corresponding values for the Battrum sample are almost three times lower. This discrepancy is almost certainly due to the inclusion of inorganic salts in the recovered product. Because of the high solubility of water in ethyl acetate, a fraction of the aqueous permeate containing high concentrations of dissolved salts (Table 5) ended up in the extracted phase. Subsequent removal of the ethyl acetate and water then left the salts with the organic extract.

Because of the limited amount of sample available for the various analyses, few nitrogen and sulfur analyses could be performed. The available data seem to confirm, however, the earlier findings (Section 3.3.1) that the nitrogen and sulfur contents are low. Also shown in Table 12 in an additional column is the weight percentage of elements other than carbon and hydrogen (100-C-H); oxygen is expected to make up the bulk of this fraction, the exception being the Battrum sample with its high salt content.

The carbon to hydrogen ratios are all higher than the C/H ratios found for the residues from the raw permeates, confirming that traces of water must have been present in the latter samples. The relative positions of the C/H ratios for the various ethyl acetate extracts are, however, very similar to those for the permeate residues. The Battrum sample is again the most aromatic, followed by the Fosterton sample. The Eyehill C/H ratio, just above the average C/H ratio for the various steamflood permeate residues, is now found below the Lone Rock value and hence the Eyehill extract would be the most aliphatic.

Looking ahead at the ^{13}C NMR and GC/MS results in Sections 3.5.6 and 3.5.7, which show that the extracts mostly consisted of aliphatic carboxylic acids, benzoic acids and phenols in various proportions, the elemental analyses and C/H ratios found for these extracts compare very well with the NMR and GC/MS findings. Aliphatic carboxylic acids and esters have C/H ratios of 0.5, whereas at the other end aromatic compounds such as phenols and benzoic acids have C/H ratios >1. Mixtures such as represented by the composite compound dihydroxyphenyl pentanoic (valeric) acid, all of whose features are observed in the Fosterton sample, would have a C/H ratio of 0.83, contain 61.2 wt % C, 6.1 wt % H and 32.7 wt % O, and have an average molecular weight of 196. These figures are in excellent agreement with the actual Fosterton results.

Considering the similarity between the NMR spectra of the Eyehill and Fosterton extracts, the lower C/H ratio and molecular weight of the former come somewhat as a surprise. The presence of ethyl acetate solvent would tend to lower the values of these properties, but NMR showed no trace of the solvent. With the exception of the Eyehill case, the trend of the C/H ratio towards increasing aromaticity as one goes from the steamflood samples to the fireflood samples, with the Battrum sample being the most aromatic, is confirmed by the NMR and GC/MS results.

3.5.2 Molecular Weight

The average molecular weights of the ethyl acetate extracts as determined by vapour pressure osmometry (VPO) are shown in Table 12. Because the Battrum sample contained possibly up to 61% inorganic salts, the as-determined molecular weight could be 156% higher than the actual molecular weight of the organic fraction. Using this figure to correct the as-determined value of 242, a minimum molecular weight of 95 is obtained for the Battrum sample, if the salt did not interfere with the VPO measurement. (If the salt contributed to the VPO readings, the actual molecular weight would have been higher.) This estimated Battrum molecular weight falls below the Fosterton and Lone Rock values of 199 and 184, respectively, but is close to the Eyehill molecular weight of 125.

Molecular weights derived from VPO must be viewed with caution. Depending on the solvent, ionization may take place, which would lead to apparent molecular weight values that are falsely low, whereas dimerization, agglomeration or incomplete dissolution would yield falsely high values. Because of the acidic nature of the ethyl acetate extracts and the basic character of the pyridine solvent used, straight ionization of the solute was not expected to be a problem. On the other hand, solute-solvent association or even incomplete dissolution (due to the large sample sizes used in the VPO measurements) may have taken place. Hence, the as-determined molecular weights should be considered upper limits of the actual molecular weights.

3.5.3 Acid Number

The results of titrating solutions of the ethyl acetate extracts with potassium hydroxide (acid number determination) are shown in Table 12. The total acid numbers are broken down into three components, i.e. very strong acids (corresponding to mineral and sulfonic acids), strong acids (carboxylic acids) and weak acids (Lewis acids such as phenols).

The three fireflood samples show contributions by the strong component only, sugggesting that these (oxydized) samples mainly consisted of carboxylic acids. The Battrum acid number is 2 to 2.5 times higher than the Eyehill and Fosterton samples, in line with the NMR results that the Battrum sample consisted almost entirely of carboxylic acids. The Eyehill and Fosterton samples also contained other compounds than carboxylic acids, such as phenols. Since no weak acids were observed, it is possible that the phenols these samples contained were too weakly acidic to be detected by the acid number determination.

The Lone Rock steamflood sample is distinct from the fireflood samples in that it has a somewhat lower strong acid number component and a sizeable weak acid component. The mole rate of carboxylic acids to phenols based on the acid number values (3.6) is much lower than that implied by the NMR data (5.4) from Table 18. This would suggest that the NMR results should be considered as approximate only.

3.5.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was employed to determine the thermal stability of the ethyl acetate extracted organic materials. The results of the TGA tests in a non-oxidizing atmosphere (nitrogen) are shown in Table 13, together with an interpretation of the observed events. TGA data can only be useful to estimate thermal events such as evaporation or chemical decomposition in a given temperature range. Because the experiments were carried out in an open flow system, the sometimes complex TGA behaviour cannot distinguish between these two types of events without the aid of a known reference or standard surfactant. Ideally, differential scanning calorimetry (DSC) in a closed cup with a nitrogen atmosphere would be the thermal analysis method of choice for these samples. From the signs of the heat of reaction of model compounds, the assignments of evaporation and decomposition events may then be carried out more meaningfully. Such experiments, however, would have been well outside the scope of the determination originally envisaged.

Defining for the purpose of this study thermal stability to include the combined effects of evaporation and chemical decomposition (as measured by the weight loss in TGA), the following thermal stability data are obtained.

	50% Weight Loss	80% Weight Loss
Battrum	290°C	475°C
Eyehill	170°C	225°C
Fosterton	240°C	340°C
Lone Rock	440°C	>800°C

The Eyehill sample was clearly the least stable (or most volatile) of the four extracts tested, an apparent agreement with the finding that it also had the lowest molecular weight. At the other extreme was the very stable Lone Rock sample, which had only lost 65% of its weight when the experiment was terminated at 800°C. The stabilities of the Fosterton and Battrum samples fell in between these two extremes, but were closer to the Eyehill value.

Table 13. Thermogravimetric Analysis of Ethyl Acetate Extracts in Nitrogen

Sample	Number of Events	Temperature Range of Events °C	Observations
Battrum	≈3	150-250 250-350 350-460	Higher boiling point compounds. First 2 events due to evaporation. The second is probably complex mixture. The third event at 440°C indicates decomposition.
Eyehill	≈3	80-200 200-230 230-270	Events are not well resolved. They are probably due to evaporation processes of at least 3 compounds rather than to decomposition. More volatile than others. No evidence of decomposition.
Fosterton	≈5	100-210 210-260 260-340 340-370 400-500	First 3 peaks probably due to evaporation; peaks at 350°C and 460°C probably due to decomposition.
Lone Rock	≈3	100-200 200-340 360-500	First peak evaporation. The complex second event could reflect evaporation and low thermal stability of other constituents. The third event at 450°C is probably due to decomposition.

3.5.5 Infrared Analysis

The infrared spectral data on the five ethyl acetate extracts are listed in Table 14.

a) Presence of Solvent

Infrared absorption bands for the ethyl acetate solvent are included in Table 14. These bands are expected to be small contributors to the extract spectra. Although all absorption bands of ethyl acetate are present to some extent in the spectra of the five samples, this does not necessarily confirm the presence of ethyl acetate as other compounds, such as carboxylic acids, absorb in the same regions. It was concluded, for instance, that the absorption bands at 1705-1700 cm^{-1} were composed of compounds other than just ethyl acetate. This was determined by comparing the absorbance intensity ratios of the 1700 cm^{-1} and 1370 cm^{-1} bands. In addition, ethyl acetate would also be expected to absorb at higher frequencies in the 1700 cm^{-1} band (1735-1746 cm^{-1}). Thus, the presence of ethyl acetate can be neither excluded nor confirmed, and the amount of its absorbance contribution, if any, remains unknown.

b) Functional Groups

The spectra of the five extracts are again very similar, with the Battrum and Eyehill spectra exhibiting additional weak peaks due to thicker or more concentrated samples.

The most notable difference in the infrared spectra of the ethyl acetate extracts, when compared to those of the dried residues from the raw permeates, is the emergence of the strongly absorbing C=O stretch at 1705-1700 cm^{-1}. This band is attributed mainly to carboxylic acids, although other carboxyl compounds may also contribute. The interpretation that carboxylic acids are responsible for the majority of features in these spectra is also supported by the shift of the O-H stretching band towards lower

Table 14. Infrared Absorption Data of Ethyl Acetate Extracts

Wavenumber(cm^{-1})						
Firefloods			Steamfloods		Ethyl Acetate	Vibrational Mode
Battrum	Eyehill	Fosterton	Lone Rock	Meota		
3000	3200	3100	3200	3200		- Carboxylic acid O-H stretch; phenol or alcohol O-H stretch
	2960,2930	2960,2930	2955,2920	2960,2920	2990,2945	- C-H stretch
	2870	2870	2870	2880	2910	
2660,2550	2670	2660	2640 sh	2640 sh		- Thio-compounds S-H stretch
1700	1705	1705	1700	1700	1736	- Carboxylic acid C=O stretch; ethyl acetate
1600	1605,1595 1515,1500	1605	1600	1600		- Carboxylic acid anion C=O stretch; aromatic skeletal vibrations; olefin C=C stretch
1450	1470,1450	1455	1450	1430		- Aromatic skeletal vibrations; C-H bending
1420	1420	1415				- Carboxylic acid COH in-plane bending; carboxylic acid anion CO_2 symmetric stretch; carbonate ion CO asymmetric stretch; C-H bending
1370	1380	1385	1370	1370	1375	- Ethyl acetate; C-H bending
1290	1285	1285	1270	1280		- Carboxylic acid dimer CO stretch
1230 sh	1240	1240	1230	1240	1243	- Ethyl acetate
1075	1110,1070	1130,1070	1090 sh	1100		- Phenol or alcohol C-O stretch; aromatic ring C-H bending
					1043	- Ethyl acetate
	940	930	950	950		- Carboxylic acid OH out-of-plane bending
890	885	890	880			- Carbonate ion CO_3 deformation out-of-plane
	810					- Unassigned
760	755	760	760	760		- Unassigned
730,715	715	715				- Unassigned
685	690	685				- Unassigned
660	660	660				- C-H bending; carbonate ion CO_3 deformation in-plane
640,610						

sh - shoulder

frequencies. Formerly centered at 3480-3400 cm^{-1}, this band now attains its maximum absorption at 3200-3000 cm^{-1}. Another interpretation for this shift could be that the ratio of carboxylic acids to phenols has increased compared to the permeate residues. Dimerization of acids and intramolecular H-bonding also tend to shift the absorption band of the O-H stretching mode to lower frequencies. Other bands due to carboxylic acids might include 950-930 cm^{-1} (out-of-plane bending of OH), 1290-1270 cm^{-1} (C-O stretch for dimeric acids), and 1440-1415 cm^{-1} (in-plane bending of COH).

Some carboxylic acids may still be present in anionic form as evidenced by the bands at 1605-1600 cm^{-1} and 1420-1415 cm^{-1}. The width of the latter band, similar to the width of the 1700 cm^{-1} band, supports its assignment as CO stretching for carboxylic acid anions.

Any phenols or alcohols present would absorb at approximately 3480-3400 cm^{-1} and 1130-1060 cm^{-1}, and hence are probably present, perhaps to a lesser degree than the acids.

Thio-compounds are again indicated by the weak, but usefully located S-H stretch absorption band at 2670-2650 cm^{-1}, which is present in all five spectra. Likely, these compounds occurred in too low a concentration in the permeate residues for this band to be observed.

c) Spectral Differences Between Individual Samples

The appearance of the additional weak bands in the Battrum and Eyehill spectra are attributed to concentration or sample thickness differences. Some absorption intensity ratio differences across the spectra do occur. Most probably, the same classes of compounds are present in all extracts but in varying proportions.

The location in the Eyehill, Lone Rock and Meota spectra of the O-H stretch band at a higher frequency (3200 cm^{-1}) than in the Battrum and Fosterton spectra (3000 cm^{-1} and 3100 cm^{-1}, respectively) possibly indicates a higher ratio of phenols to carboxylic acids in these three extracts.

3.5.6 ^{13}C NMR Spectroscopy

A) Introduction

The measurable parameters from a NMR experiment are (1) chemical shifts, (2) integrated peak areas, (3) coupling constants, and (4) the spin-lattice (T_1) and spin-spin (T_2) relaxation times. The chemical shift is the position of a resonance signal (measured in ppm) with respect to a reference signal, commonly (and throughout this report) that of tetramethylsilane (TMS). The chemical shift of an atom (or rather nuclear spin) is a function of the electronic environment around that particular nucleus. Since, unless symmetry is involved, each atom within a molecule generally has a unique electronic environment, the chemical shift is a qualitative indicator of the atom type within a molecule. The area under a resonance signal is directly related to the number of atoms (spins) having the same electronic environment and can be used for quantitative measurements under certain conditions. The coupling constant, a measure of the dipolar interaction between neighbouring nuclear spins, manifests itself in the splitting of the resonance signals. It may be used to obtain information about the number and type of atoms adjacent or attached to the atom being observed. The relaxation times are time constants for the rate processes involved when the nuclear spins re-establish equilibrium after being inverted. Although not routinely used, these are useful molecular dynamic parameters and have been applied, for instance, to resolve and quantify constituents in complex mixtures (spin grouping).

The use of both ^{1}H and ^{13}C high-resolution NMR spectroscopy for qualitative and quantitative analysis and characterization in fossil fuel chemistry has expanded considerably during the past two decades.[93] ^{1}H and ^{13}C spectroscopy are mainly employed to assign structural units characteristic of hydrocarbons. ^{1}H NMR spectroscopy was first used for this purpose, especially because it provided a clear distinction between the aromatic and saturated protons. The use of ^{1}H NMR for further qualitative analysis is, however, severely limited by the narrow range of the chemical shifts, which results in broad, unresolved signals, and by the difficulties encountered in converting the hydrogen structure to the basic carbon skeleton. In addition, information on quaternary carbons, which can be present in significant amounts, cannot be obtained. Because of these drawbacks, ^{13}C spectroscopy rapidly gained popularity when the pulse excitation Fourier transform technology became available. ^{13}C NMR spectroscopy provides direct observation of the carbon structure with generally well-resolved lines, which due to the extreme sensitivity of the resonant carbon nucleus to molecular geometry are spread over a wide range of chemical shifts (the spectral width in ^{13}C NMR is more than twenty times larger than in ^{1}H NMR). As was the case in ^{1}H NMR spectroscopy, extremely complicated spectra may arise, especially in mixtures, as carbon resonances are usually split--in this case because of proton-carbon couplings--and tend to overlap. However, unlike the proton-proton couplings in ^{1}H NMR, these proton-carbon couplings and thus the signal splittings can be eliminated by broadband decoupling of the ^{1}H nuclei, greatly simplifying the spectra for interpretation. Proton decoupling has the added benefit that signal enhancement is obtained not only by collapsing the line multiplets, but also through dynamic polarization of the carbon nuclei (nuclear Overhauser effect [NOE]).

Because of the much better resolution of ^{13}C NMR spectra, ^{13}C spectroscopic analysis of the ethyl acetate extracts was selected as the preferred NMR method. Not only does it provide more qualitative information than proton NMR under certain conditions, this information can also be quantitative. These conditions relate to two inherent problems in obtaining quantitative results from a normal, proton-decoupled, pulsed FT ^{13}C NMR spectrum, i.e. the long relaxation times of carbon atoms, in particular quaternary carbons, and the unequal nuclear Overhauser effects of different types of carbon nuclei. Regarding the first problem, in order to obtain quantitative results, the carbon nuclei must all be fully relaxed before a repetitive pulse can be applied. The long relaxation times would, however, result in undesirably long experimental times. Fortunately, the addition of paramagnetic metal complexes, such as the chromium(III) triacetylacetonate used in the present experiments, reduces the relaxation times drastically, allows pulses to be repeated at short time intervals, and thus reduces measuring times. The second problem, unequal Overhauser enhancements, can be eliminated by gating the decoupler field, with the decoupler on during data acquisition and off during the pulse and delay times. In the present analyses gated decoupling was accomplished with the microprogram NONOE. With the fulfillment of the two conditions, short relaxation times and the elimination of NOE, reliable quantitative data were obtained in relatively short measuring times.

With respect to the above four types of parameters that may be extracted from an NMR experiment, within the scope of this project only the chemical shift and peak integration parameters were investigated.

B. ^{13}C NMR Chemical Shifts and Peak Integration Values

^{13}C NMR spectra of hydrocarbons are generally divided into two distinct parts: the aliphatic region, 0-70 ppm, and the aromatic regions, 110-160 ppm. Signal integration over these two regions is often performed to determine the aromatic/aliphatic ratio (aromaticity) of fossil fuels. A third distinct region, the carbonyl region from 160-220 ppm, becomes important and must be added when oxygenated hydrocarbons are involved. The above regions can be further subdivided into several bands, as shown in Table 15. Different workers[94-96,98-100] in this field have used different division schemes as a consequence of the mutual overlap of the subregions. Therefore, the indicated subdivisions are approximate. With respect to compounds containing heteroatoms, only oxygen-functional groups are included in the following discussions as the elemental analyses showed that

Table 15. ^{13}C NMR Chemical Shifts

Hydrocarbon Type	Chemical Shift (ppm from TMS)	Assignment	
Saturated			
Aliphatic	0-70	C_{al}	Aliphatic (paraffinic) carbons
	14.1	C_α	α-Carbons in straight-chain alkanes (CH_3)
	19.7		Methyl side chains (branched alkanes)
	18-21		Methyl carbons on aromatic rings
	20-45		Secondary-quaternary carbons in branched alkanes.
	22.9	C_β	β-Carbons in straight-chain alkanes (CH_2)
	29.7	C_n	δ or further removed carbons in straight-chain alkanes (CH_2)
	32.2	C_γ	γ-Carbons is straight-chain alkanes (CH_2)
Alicyclic	20-45	C_{ac}	Alicyclic (naphthenic) carbons (CH_2, CH)
Alcohols, Ethers, Esters	40-65	C_{al-O}	Carbons joined to hydroxyl or alkoxyl (ether groups)
	60-75		Aryl-alkyl ethers
Unsaturated	70-150	C_{uns}	Unsaturated (olephinic) carbons in alkenes and alkynes
Aromatic	110-160	C_{ar}	Aromatic carbons
	110-130	C_{ar-H}	Aromatic protonated carbons
	110-120	$C_{ar(o)-O}$	Aromatic carbons ortho to hydroxyl or alkoxyl substituents
	123-126	$C_{ar-ar-ar}$	Carbons at the junction of three aromatic rings
	128-136	C_{ar-ar}	Carbons at the junction of two aromatic rings
	132-137	C_{ar-ac}	Carbons at the junction of an aromatic and a naphthenic ring
	129-137	C_{ar-me}	Methyl-substituted aromatic carbons
	137-148	C_{ar-alk}	Alkyl-substituted (except methyl) aromatic carbons
	148-160	C_{ar-O}	Aromatic carbons, bearing hydroxyl or alkoxyl substituents
Carbonyl	160-220		Carbonyl carbons
	160-175		Carbonyl carbons in esters
	165-185		Carbonyl carbons in carboxylic acids
	175-205		Carbonyl carbons in aldehydes
	175-220		Carbonyl carbons in ketones

that the nitrogen and sulfur contents of the ethyl acetate extracts were small. Table 15, in conjunction with compilations of ^{13}C NMR chemical shifts of known compounds,[91-92] was used in the interpretation of the experimental data.

The ^{13}C NMR spectra of the four ethyl acetate extracts investigated (Battrum, Eyehill, Fosterton and Lone Rock) are shown in Figures A1 to A4. The computer-generated printouts of the chemical shifts were combined into Table 16. For some peaks, whose intensities fell below the limit set by the operator and which therefore did not show up in the printout, the chemical shifts were measured directly from the spectra. The relative intensities shown in Table 16 were obtained by assigning the strongest peak in each spectrum the arbitrary value of 100 units and using the computer-generated absolute intensities to calculate the relative values. Furthermore, as shown by the horizontal divisions in Table 16, most observed ^{13}C NMR chemical shifts could be grouped together in narrow ranges of ±0.3 ppm. Given that the experimental accuracy was approximately ±0.1 ppm, peaks within these ranges most probably arose from identical or nearly identical carbons. Also shown in Table 16 are general assignments pertinent to the chemical shifts observed for these samples. As indicated by the traces in Figures A1 to A4, peak areas in the carbonyl, aromatic and aliphatic regions were integrated (n.b., different amplification settings were used for the various traces). The measured values for each of these traces were converted to the same basis and added for each of the three regions. Table 17 shows the resulting carbon distributions, expressed as fractions (C_{region}/C_{total}). The aromatic fractional values represent the familiar aromaticity parameter.

The ^{13}C NMR spectra of the three ethyl acetate extracts of fireflood origin (Battrum, Eyehill and Fosterton) and the one steamflood sample (Lone Rock) are all very well dissolved, showing distinct peaks and no diffuse areas. (Due to the smaller number of accumulations the signal-to-noise ratio of the Battrum spectrum is somewhat lower than the rest.) The three

Table 16. ^{13}C NMR Chemical Shifts of Ethyl Acetate Extracts

CHEMICAL SHIFT (PPM FROM TMS)	BATTRUM		EYEHILL		FOSTERSON		LONE ROCK		Assignment
	Peak Number	Relative Intensity*	Peak Number	Relative Intensity*	Peak Number	Relative Intensity*	Peak Number	Relative Intensity*	
195.4					1	n/a			Carbonyl carbon in aldehydes or ketones
177.7			1	6					Carboxyl carbon in aliphatic carboxylic acids (172-183 ppm)
177.4							1	9	
177.2	1	34	2	15					
175.1	2	n/a							Carboxyl carbon in methyl esters of aliphatic carboxylic acids (166-175 ppm)
175.0			3	13	2	12			
174.4					3	30			Carboxyl carbon in benzoic acid (172.6-174.9 ppm)
174.3			4	41					
174.2	3	n/a	5	29	4	18			
173.6			6	9					
172.1							2	100	
171.9					5	100			
171.8	4	79	7	59					
170.3							3	11	Carboxyl carbon in alkyl acetates (167-171 ppm)
170.2					6	57			
168.5	5	73			7	8			
167.2					8	37			Carboxyl carbon in (substituted) methyl benzoates (165-168 ppm)
167.1	6	64	8	36					
166.5					9	19			
166.4	7	100							
165.8					10	17			
165.7	8	25							

* Maximum intensity 100 units.

Table 16 (continued)

CHEMICAL SHIFT (PPM FROM TMS)	BATTRUM		EYEHILL		FOSTERSON		LONE ROCK		Assignment
	Peak Number	Relative Intensity*	Peak Number	Relative Intensity*	Peak Number	Relative Intensity*	Peak Number	Relative Intensity*	
157.5	9	n/a							Aromatic carbon joined to ether oxygen
157.3					11	12	4	4	
157.2	10	30	9	44					
155.2			10	8					Aromatic carbon joined to hydroxyl substituent
145.3							5	4	
134.3	11	27							Methyl-substituted aromatic carbons (129-137 ppm)
133.5					12	11			
133.3	12	45	11	6	13	12			
132.8			12	23					
132.7	13	76			14	22			
132.3					15	10			
132.2	14	31							
132.0					16	10			
131.9			13	6	17	19			
131.8	15	46			18	20			
131.1					19	16			
131.0	16	67	14	7					
130.7	17	52							Protonated aromatic carbon; aromatic carbon substituted by CO_2H
130.6			15	34	20	26			
130.4			16	13					

*Maximum intensity 100 units.

Table 16 (continued)

CHEMICAL SHIFT (PPM FROM TMS)	BATTRUM		EYEHILL		FOSTERSON		LONE ROCK		Assignment
	Peak Number	Relative Intensity*	Peak Number	Relative Intensity*	Peak Number	Relative Intensity*	Peak Number	Relative Intensity*	
129.7	18	35							
129.5			17	21					
129.4					21	19	6	5	
129.3	19	47							
129.2			18	100	22	42			
129.1	20	64							
128.5	21	50	19	52	23	36			
128.3	22	52							
126.9			20	6					Aromatic carbon para to OPh and OAc substituents
126.5			21	10					
123.6			22	10					
119.9					24	15			Aromatic carbon ortho or para to hydroxyl or ether substituents (110-120 ppm)
119.8	23	47							
119.7					25	12			
119.3							7	4	
118.9							8	3	
118.7			23	37					
115.7			24	8	26	10	9	5	
115.6	24	23							
115.3							10	6	
115.1			25	70	27	10	11	3	
114.4			26	8					

* Maximum intensity 100 units.

Table 16 (continued)

CHEMICAL SHIFT (PPM FROM TMS)	BATTRUM		EYEHILL		FOSTERSON		LONE ROCK		Assignment
	Peak Number	Relative Intensity*	Peak Number	Relative Intensity*	Peak Number	Relative Intensity*	Peak Number	Relative Intensity*	
60.3	25	n/a							Methylene carbon adjacent to hydroxyl or ether oxygen
59.9							12	9	
59.7					28	46			
42.8			27	10					Methylene, methine or quaternary carbon in branched alkanes (20.7-41.8 ppm)
35.5			28	20	29	16			
33.5			29	15	30	17			γ+ (CH_2) carbon in straight alkanes (29.5-32.4 ppm)
33.3			30	23	31	17			
33.0			31	10					
31.1			32	8					α-Methyl in branched alkanes (19.3-31.5 ppm)
30.9			33	8					
30.7			34	10	32	9			
30.7					33	10			
28.7					34	11			Methylene carbon in ethyl substituent on aromatic ring (29.3 ppm)
28.6			35	8	35	11			
26.8			36	18	36	15			
26.5			37	20	37	13			
26.3							13	7	
26.1	26	23	38	13					
24.9			39	11					β-carbon (CH_2) in straight alkanes (22.6-23.3 ppm); β-methylene in propyl substituent on aromatic ring (25.2 ppm)
24.1			40	11	38	9			
22.1	27	n/a	41	22					
22.0					39	15			
21.8					40	13			
21.6			42	23	41	17			

* Maximum intensity 100 units.

Table 16 (continued)

CHEMICAL SHIFT (PPM FROM TMS)	BATTRUM		EYEHILL		FOSTERSON		LONE ROCK		Assignment
	Peak Number	Relative Intensity*	Peak Number	Relative Intensity*	Peak Number	Relative Intensity*	Peak Number	Relative Intensity*	
21.1							14	69	Sterically unhindered methyl substituent on aromatic ring; α-methyl to carboxylic group
21.0	28	57							
20.9			43	49	42	75			
20.8							15	14	
20.7					43	49			
20.0			44	8					
18.8			45	11	44	8			
17.9			46	16	45	11			Methyl carbon in ethyl substituent on aromatic ring (16.0-16.8 ppm); methyl group on aromatic ring with two ortho substituents (14.6-16.9 ppm); γ-methyl in branched alkanes (14.5-15.9 ppm)
16.5							16	4	
16.4	29	19	47	11					
15.8			48	9					
14.1							17	7	Methyl (α-carbon) in straight alkanes (12.7-14.1 ppm)
14.0					46	36			
13.8					47	16			
13.7			49	19					
13.6	30	n/a							
13.5			50	22					
13.5			51	22	48	16			
13.4					49	15			
11.5							18	5	β-Methyl in branched alkanes (8.4-11.5 ppm)
11.3	31	18	52	9					
9.5					50	n/a			β-Methyl to carboxylic group
9.2	32	n/a							
9.0			53	6					

* Maximum intensity 100 units.

Table 17. Carbon Type Distribution Based on Peak Integration Values

Carbon Type	Fractional Distribution by Carbon Type			
	Battrum	Eyehill	Fosterton	Lone Rock
Carbonyl	0.31	0.17	0.26	0.33
Aromatic	0.59	0.50	0.39	0.31
Aliphatic	0.11	0.34	0.35	0.36

fireflood samples exhibit a remarkable overall similarity, with multiple peaks concentrated in three distinct and separate regions (carbonyl, aromatic and aliphatic). The ^{13}C NMR spectrum of the steamflood sample, on the other hand, is relatively simple, showing considerably fewer lines, especially in the aromatic region. Again, however, resonances that do occur fall in the same three regions identified in the fireflood spectra.

The peak integration data of Table 17 further differentiate these observations. The Lone Rock sample does indeed have the lowest aromatic carbon content of all four samples, but it is somewhat surprising that with a very strong peak in both the carbonyl and the aliphatic regions the aromatic content still amounts to almost one-third of the total. The Battrum sample is the most aromatic, followed by the Eyehill and Fosterton samples. The Battrum sample also has the least amount of aliphatic carbons, whereas the Eyehill, Fosterton and Lone Rock samples have about the same number of aliphatic carbons. The carbonyl carbon content (or more precisely, the carboxyl carbon content as will be discussed below) is the highest in the Battrum and Lone Rock samples and the lowest in the Eyehill sample, with the Fosterton sample being situated in between.

a) Lone Rock ^{13}C NMR Chemical Shifts

There are three resonances in the carbonyl region of 177.4, 172.1 and 170.3 ppm. Based on published chemical shifts,[91] they can be assigned to carboxyl carbons in aliphatic carboxylic acids (approximately 172-183 ppm), in benzoic acids (172.6-174.9 ppm), in methyl esters of aliphatic carboxylic acids (166-175 ppm) and in alkyl acetates (167-171 ppm). The peak at 172.1 ppm is about ten times stronger than the other carboxyl resonances and is matched by an equally intense peak at 21.1 ppm in the aliphatic region. Lines at about 21 ppm can be assigned to sterically unhindered methyl substituents on aromatic rings or to methyl groups attached to a carboxylic group (acetyl carbon). Because of the comparatively low aromatic content, only the latter possibility should be considered. Thus, the two strong resonances may be assigned to acetic acid. Literature values, however, are 177.2 and 21.1 ppm, requiring an explanation for the lower observed value for the carboxyl carbon chemical shift. Different solvents have been shown to affect the degree of hydrogen bonding of carboxylic acids and consequently, the shielding of the carboxyl carbons.[91] This may also be the case for the solvent used here (DMSO), although no published data are available for confirmation.

In addition to the peaks in the aromatic region and the methyl and methylene carbon resonances in the aliphatic region, there is a single peak at 59.9 ppm that also occurs in the Battrum (weak) and Fosterton spectra. The region 40-75 ppm is usually assigned to O-alkyl carbons in alcohols, ethers and esters; resonances in the 60-65 ppm band may be due to primary alcohols or ethoxy (methylene carbon) esters. The literature value[91] for the methylene carbon in ethyl acetate is 60.1 ppm and closely matches the observed value of 59.9 ppm. The other literature values for ethyl acetate[91] are 169.5-170.7 (carboxyl), 20.3 (acetyl) and 14.3 (ethoxy methyl) ppm. Peaks are found at 170.3, 20.8 and 14.1 ppm, confirming the possible presence of ethyl acetate. Since ethyl acetate was the extracting solvent, incomplete removal of the solvent (as indicated by the ethoxy resonance at 59.9 ppm) is the likely reason for its presence.

In the aliphatic region, there remain three peaks at 26.3, 16.5 and 11.5 ppm to be assigned. The resonances at 26.3 and 11.5 may be due to an ethyl group attached to a deshielding group (β alkyl carbons normally appear at 22.6-23.3 ppm). A combination with the unassigned carboxyl peak at 177.4 could point to propionic acid (literature values 180.4, 27.8, 9.0 ppm). Again, the shift changes may be due to hydrogen bonding or other solvent effects.

A relatively small number of resonances appear in the aromatic region (110-160 ppm). The chemical shift range of 148-160 ppm mainly contains resonances diagnostic for aromatic carbons joined to hydroxyl and ether oxygen groups, while the range 110-120 ppm contains protonated aromatic carbons ortho (or para) to these groups. All aromatic resonances, with the exception of the signal at 129.4 ppm, fall in these two ranges suggesting a strong presence of phenolic and/or alkyl-aryl ether compounds. The peak at 129.4 ppm is at the upper limit for protonated aromatic carbons and could be due to the carbon meta to the above hydroxyl or ether groups. All peaks in the 110-130 ppm range are split or composite, indicating the presence of a number of very similar phenolic compounds. According to literature data,[91] phenol resonates at 155.6 (C-1), 130.8 (C-3), 120.8 (C-4) and 116.1 (C-2) ppm. The Lone Rock sample shows resonances at 157.3, 129.4, 118.9-119.3 and 115.1-115.7 ppm, confirming the presence of phenol. The presence of anisole (methoxybenzene), another phenolic compound with similar aryl resonances, is excluded because of the lack of the characteristic methoxyl resonance at 54.0 ppm.

There remain two unassigned signals, one aromatic at 145.3 ppm and one aliphatic at 16.5 ppm. The 145.3 ppm resonance falls in the range for alkyl (non-methyl) substituted aromatic carbons, but alkyl substitution is not likely because of the absence of α-methylene alkyl carbons (e.g. α-methylene in ethylbenzene resonates at 30.0 ppm).[103] Assignment of this resonance to a diphenol is a good possibility. Seshadri and Cronauer[101] assigned signals near 146.3 ppm to quaternary carbons in unspecified diphenols, while Johnson, LeRoy and Jankowski[92] determined the chemical shifts of catechol (1,2-dihydroxybenzene) as being 145.0 (C-1), 122.1 (C-3) and 117.3 (C-2) ppm. The resonance at 16.5 ppm could be due to β-methyl in an ethyl substituent on an aromatic ring (16.0-16.8 ppm) or to an aromatic methyl group with two ortho substituents (14.6-16.9 ppm). As ethyl substitution was just excluded, the latter possibility, resulting in the postulation of 2,6-dihydroxytoluene (a diphenol), is realistic and would also account for the splits in the 110-130 ppm resonances. Finally, the presence of cresols (hydroxytoluenes) can also be excluded. One of the resonances of m-cresol occurs at 139.0 ppm (C-3), while o- and p-cresol have resonances near 124.0 ppm (C-2, C-6); both resonances are not observed in the Lone Rock sample.

b) Battrum ^{13}C NMR Chemical shifts

Compared to the Lone Rock spectrum, the Battrum spectrum is considerably more complicated in the carbonyl and aromatic regions. The complex peaks in the latter region are also much more intense and have line integrals similar in magnitude to those in the carbonyl region. Despite these differences, several of the compounds tentatively identified from the Lone Rock spectrum are also present in the Battrum sample.

The resonances at 177.2, 26.1 and 11.3 ppm may be assigned to propionic acid, those at 171.8 and 21.0 ppm to acetic acid, those at 60.3 and 13.6 ppm to a trace of ethyl acetate (carboxyl and acetyl carbons are not detected), and those at 157.2, 130.7, 119.8 and 115.6 ppm to phenol. The Lone Rock peak at 145 ppm is not present in the Battrum spectrum.

In the carbonyl region a series of closely spaced intense peaks can be observed slightly upfield (165.7-168.5 ppm) from the 171.8 ppm resonance assigned to the carboxyl carbon in acetic acid. Table 15 indicates that this is the resonance band for esters of carboxylic and benzoic acids. However, the absence of any matching peaks in the alkoxy band, primarily 50-65 ppm, rules out the presence of esters. Carboxylic acids longer than acetic acid can also be excluded, since they resonate downfield from acetic acids and no matching alkyl resonances of comparable intensities can be found. Hence, these carbonyl resonances have been assigned to a series of substituted benzoic acids. Solvent effects and/or hydrogen bonding may again be the reason for the general upfield shift of the carboxyl carbon resonances in these acids. (The literature value for this resonance in benzoic acid is 172.6-174.9 ppm.[91-92]) The literature values for the resonances of the aryl carbons in benzoic acid are 133.7 (C-4), 130.2 (C-2), 129.4 (C-1) and 128.4 (C-3) ppm. As several close matches can be found in the Battrum spectrum for each of these aryl resonances, strongly suggesting a one-to-one correspondence with the various carbonyl resonances tentatively assigned to benzoic acid and its substituted derivatives, the presence of these compounds may be considered confirmed. A number of weak to very weak resonances in the aliphatic (22.1, 16.4, 13.6 and 9.2 ppm) and carbonyl (174-175 ppm) regions remains unassigned. As discussed in more detail with the Eyehill sample, most of these resonances are likely due to small amounts of aliphatic carboxylic acids. The signals at 22.1 and 16.4 ppm may also arise from methyl substituents on aromatic ring structures, further confirming the presence of methyl-substituted benzoic acids.

c) Eyehill ^{13}C NMR Chemical Shifts

The Eyehill spectrum shows fewer resonances in the carbonyl region than the Battrum spectrum, with a concomitant decrease in the aromatic region. The aliphatic region is considerably more complex, with several resonances overlapping or split. Comparison with the previously assigned resonances shows that the following compounds are likely present: propionic acid (weak signals at 177.2-177.7, 26.5-28.6 and 11.3 ppm), acetic acid (strong signals at 171.8 and 20.9 ppm), phenol (strong signals at 157.2, 129.2, 118.7 and 115.1 ppm) and benzoic acid (identified from the medium-strong signals at 167.1, 132.8, 130.6, 129.5 and 128.5 ppm). There was no trace of ethyl acetate (absence of 50-60 ppm resonances). The presence of only benzoic acid, without substituted derivatives, simplified the carbonyl range and reduced the complexity of the aromatic band. The small peak at 155.2 ppm and minor satellites of the phenol peaks at 118.7 and 115.1 ppm point to the presence of substituted phenols in small quantities. The resonance at 123.6 ppm indicates that these phenols could be o- or m-cresol.[101]

The aliphatic portion of the spectrum is complex and spread over a wider range (9-43 ppm) than the previous two samples. Resonances in this range are primarily due to methyl and methylene carbons in longer aliphatic chains or branched aliphatic chains. Resonances in the range 20-45 ppm may also be due to alicyclic compounds. Substitution of these alkyl chains in aromatic rings is unlikely because of the lack of aromatic signals in the 137-148 ppm range (alkyl substituted aryl carbons). Several carbonyl resonances (174-177 ppm) have not yet been assigned, however, so the possibility of the presence of higher carboxylic acids should be investigated. (As was the case for the Battrum sample, the presence of esters can be ruled out because of the absence of alkoxy resonances in the 40-60 ppm range.) Literature values[91] for n-butyric acid are 179.6 (C-1), 36.3 (C-2), 18.5 (C-3) and 13.4 (C-4) ppm; for pentanoic (n-valeric) acid 179.7 (C-1), 34.1 (C-2), 27.0 (C-3), 22.0 (C-4) and 13.5 (C-5) ppm; and for hexanoic acid 181.0 (C-1), 34.5 (C-2), 25.2 (C-3), 32.6 (C-4), 23.7 (C-5) and 14.8 (C-6) ppm. All of the aliphatic resonances occur in the Eyehill spectrum, but the listed carboxyl carbon chemical shift values are 3-6 ppm higher (downfield) than the observed resonances. Solvent effects may again be responsible for these shifts.

Although the above carboxylic acids would account for the majority of the observed aliphatic peaks, groups of peaks around 43, 31, 26, 16-20 and 9 ppm remain unassigned. These resonances are likely due to branched alkyl groups in carboxylic acids such as i-butyric acid, i-valeric acid, etc. The lack of published chemical shift data on the latter acids precludes a positive identification.

d) Fosterton ^{13}C NMR Chemical Shifts

The Fosterton spectrum has elements of both the Battrum and the Eyehill spectra. The carbonyl and aromatic regions in the Fosterton spectrum are very similar to those in the Battrum spectrum (ignoring line intensity differences), whereas the aliphatic region is nearly identical to that in the Eyehill spectrum. There is one obvious difference, however. The characteristic ethoxy resonance at 59.7 ppm, which was earlier encountered at 59.9 ppm in the Lone Rock spectrum (while being barely observable in the

Battrum spectrum and nonexistent in the Eyehill spectrum) and assigned to ethyl acetate, is strongly present in the Fosterton spectrum. Sharp, intense resonances at 170.2, 20.7 and 14.0 ppm closely match the previous Lone Rock values and confirm the presence of ethyl acetate, the extracting solvent left behind after incomplete removal.

Assignment of the majority of the other peaks is fairly straightforward because of the similarities with the previous spectra. The following resonances can be assigned: acetic acid (strongest peaks in spectrum, at 171.9 and 20.9 ppm), phenol (157.3, 129.4, 119.7-119.9 and 115.1-115.7 ppm), benzoic acid and substituted derivatives (weak to medium-strong peaks in the carbonyl [165.8-168.5 ppm] and aromatic [128.5-133.5 ppm] regions). The phenol ortho and para resonances at 115-116 and 119-120 ppm, respectively, occur as doublets, indicating the presence of another phenolic compound with a C-1 resonance essentially identical to that of phenol (there is a slight shoulder on the C-1 resonance in the Fosterton spectrum). Peaks characteristic for cresols do not occur, however.

Following the assignment of the sharp peaks in the aliphatic region to acetic acid and ethyl acetate, the remainder of the peaks in this region closely resemble, in shape and intensity, the pattern of the aliphatic resonances found in the Eyehill spectrum. The presence in the Fosterton spectrum of almost the same set of carbonyl resonances (at 174-175 ppm) as found in the Eyehill case then leads to the same assignment of a series of aliphatic carboxylic acids. The absence in the aliphatic region of some lines below 17 ppm (e.g. 9-11 and 15-17 ppm), which can be assigned to many types of pendant methyl groups, especially in branched alkyl chains, suggests that branched carboxylic acids occur in lower proportions than they did in the Eyehill sample.

Finally, the Fosterton spectrum shows a single, small carbonyl resonance at 195.4 ppm, within the band (195-200 ppm) where one expects the carbonyl carbon of alkylphenylketones to be located. (Saturated aldehydes and ketones are generally found well over 200 ppm and aromatic aldehydes [benzaldehydes] at lower values, around 191 ppm.) Literature values for the carbonyl resonances in benzophenone and its methyl-substituted derivatives are 195.5-196.0 ppm,[91] but benzophenone itself must be excluded. Shift values for its aryl carbons include at the high end 136.6 ppm for C-1, a resonance that does not occur in the Fosterton spectrum. Since ortho and para methyl substituents generally tend to reduce the chemical shift values of C-1 resonances (upfield shifts) and many resonances are present in the Fosterton spectrum below 134 ppm (the chemical shift range for methyl-substituted aryl carbons), the carbonyl resonance at 195.4 ppm is assigned to o- or p-methylbenzophenone. The alkyl resonances of this compound are expected around 18-21 (methyl substituent) and 25-31 (acetyl group) ppm.[91] Several resonances occur in each of these ranges in the Fosterton spectrum, further reinforcing the above identification.

Conclusions

A summary listing of the compounds identified in the four ethyl acetate extracts is given in Table 18. Since it is of considerable interest to know approximately in which proportions these compounds are present, an attempt has been made to semiquantify these results.

The quantitative distributions of variously bonded carbon atoms can in principle be determined from ^{13}C NMR integrated line intensities if the conditions described in the introduction of this section are fulfilled. However, crowding and mutual overlapping of resonances arising from various carbons within the same molecule as well as from other molecules make it generally impossible to use the integration data for the calculation of the distribution of individual compounds. Integrated line intensities are, therefore, mostly used to provide quantitative information on the overall distribution in the sample of carbon types whose resonances occur in distinct and separated regions of the spectrum (usually the aliphatic, aromatic and carbonyl regions, see Table 17).

Table 18. Composition of Ethyl Acetate Extracts as Determined by ^{13}C NMR

Compound	Battrum		Eyehill		Fosterton		Lone Rock	
	Present	Mol %	Present	Mol %	Present	Mol %	Present	Mol %
Acetic Acid	+	10	+	20	+	23	+	68
Propionic Acid	+	8	+	10	Trace		+	7
Butyric Acid	+	4	+	28	+	23		
Valeric Acid	+		+		+			
Caproic Acid	+		+		+			
Branched Carboxylic Acids	?		+		+			
Ethyl Acetate	Trace		-	Nil	+	13	+	10
Aliphatic Compounds		22		58		59		85
Benzoic Acid	+	72	+	20	+			
Substituted Benzoic Acids	+				+	37		
Phenol	+	6	+	21	+	5	+	9
2,6-Dihydroxytoluene							+	5
o- and p-Cresol			+					
Other Substituted Phenols					+			
Aromatic Compounds		78		41		42		14
Methylacetophenon					+	Not Integrated		
Total Carboxylic Acids		94		78		83		75
Total Phenols		6		21		5		14

However in the case of these ethyl acetate extracts, a more detailed breakdown by compound or compound group is possible, because of the fact that almost all of the molecular species identified in the extracts either contain one carbonyl or one hydroxyl group (the only exemption being the compound identified as 2,6-dihydroxytoluene in the Lone Rock sample). Since the carbonyl and hydroxyl-bearing carbon atoms gave rise to distinct resonances that could be integrated individually or in small groups, the distribution of the various compounds identified in the sample was approximated by equating it to the distribution of the corresponding carbonyl and hydroxyl-bearing carbon atoms. (For 2,6-dihydroxytoluene only half of the integrated line intensity was taken into account.)

The resulting distributions, expressed in mole percent, are shown in Table 18. Although no direct comparison is possible, indirectly there is generally good agreement with the overall distributions by carbon type (Table 17), which were obtained by integrating all resonances in the respective spectra. Using the highly aliphatic Lone Rock sample as an example since each individual compound could be quantified in this case, one would obtain the following fractional carbon distribution based on the compound distribution of Table 18: aliphatic, 0.41; aromatic, 0.29; and carbonyl, 0.30. Given the errors in the integrated intensities, these results are in very good agreement with the values of Table 17. No such direct comparison is possible for the other samples, but it is obvious from Table 18 that Battrum is the most aromatic and least aliphatic sample, while the Eyehill and Fosterton samples are situated in between, in agreement with the data from Table 17.

A second, albeit simplistic, check can be made by analyzing the aliphatic/carbonyl carbon ratio (C_{al}/C_{carb}) based on Table 17. This parameter has the values 0.35, 2.00, 1.35 and 1.09 for the Battrum, Eyehill, Fosterton and Lone Rock samples, respectively. Assuming based on the spectral analyses that the carbonyl carbons are contained in carboxylic groups only, which must be linked either to alkyl groups (with $R \geq 1$) or aromatic rings, a value of $C_{al}/C_{carb} < 1$ would, after combining all available aliphatic carbons with carboxyl carbons, imply an excess of carboxylic groups. These carboxylic groups must thus be bonded to aromatic rings, resulting in the formation of benzoic acid-type of compounds (Battrum is a typical example). At a value of $C_{al}/C_{carb} = 1$ (e.g. Lone Rock) the number of aliphatic and carboxyl carbons is equal, suggesting the presence of mostly acetic acid. For the two remaining samples (Eyehill and Fosterton) there are more aliphatic carbons per carboxylic group ($C_{al}/C_{carb} > 1$) and hence the presence of longer-chain carboxylic acids may be implied. These very approximate conclusions are again in good agreement with the actual compositions given in Table 18.

Several possibilities exist to more fully extract all the information NMR can provide. ^{1}H NMR can be performed, for instance, to help confirm or further elucidate the sometimes somewhat ambiguous alkyl and aryl assignments from ^{13}C NMR. Having established correlations between the carbon and hydrogen contents by means of a common internal standard, the combination of ^{1}H and ^{13}C measurements can be used to extract important parameters, e.g. the overall carbon to hydrogen ratio C/H or the C/H ratios restricted to specific parts of the spectrum.[94-100,104,105] Another very promising approach in ^{13}C NMR to determine carbon C, CH, CH_2 and CH_3 group abundances (multiplicities) is the use of modern, selective pulse techniques, which can differentiate between primary, secondary, tertiary and quaternary carbons and obtain separate subspectra for each type of carbon. Examples of such pulse sequences are SEBBORD (spin echo broad band off-resonance decoupling) for investigating ^{13}C NMR resonances from non-protonated aromatic carbon sites,[106] GASPE (gated spin echo) for the determination of any carbon multiplicity (C, CH, CH_2, CH_3),[107] DEPT (distortionless enhancement by polarization transfer)[108] or the two-dimensional J-modulated spin echo technique.[109] Good quantitative results for all carbon types are claimed by the latter two techniques.

Finally, the possibility of humic and fulvic acids contributing to the

^{13}C NMR spectra of the ethyl acetate extracts has been briefly examined. Humic and fulvic acids have been found to be present in soils, coal and natural water, and there is speculation that they also might be present in produced oilfield water.[11,22-26] Preston and Blackwell recently reported ^{13}C NMR analyses of a humic and a fulvic acid from mineral soil.[110] The humic acid spectrum was characterized by four broad envelopes with sharper peaks superimposed. These envelopes occurred in the aliphatic (10-48 ppm), carbohydrate (48-105 ppm), aromatic (105-165 ppm) and carbonyl (165-190 ppm) regions. The carbohydrate region was the most intense, dominated by sharp maxima between 59 and 76 ppm. The fulvic acid spectrum was quite different, with little intensity in the aliphatic or aromatic regions. Again, however, the carbohydrate region was the most intense, displaying large peaks between 64 and 103 ppm, indicative of a high carbohydrate content. In both spectra the carbonyl signals were assigned to carboxyl, amide and ester carbons. Gerasimowicz and Byler examined solid humic acid samples extracted from sludges found in a large waste treatment process.[111] All ^{13}C NMR spectra gave rise to a dominant, unresolved signal at 30 ppm, corresponding to methyne, methylene and methyl group carbons. This peak was attributed, in part, to algal and microbial components comprising these humic substances. A second spectral region centered around 54 ppm, and was indicative of methoxyl groups (carbohydrates) derived from lignin-like structures. All the samples also exhibited aromatic character through resonances around 135 and 155 ppm. Finally, carboxyl carbons were seen in all the spectra at ca. 180 ppm; the carboxylic content decreased as the aromaticity increased. No specific compounds were identified in either of these two publications.

Because of the variable nature of humic and fulvic acids, comparison with the four ethyl acetate extracts is difficult, if not impossible. However, if the above humic and fulvic acids are representative of their class, it appears that the presence of a carbohydrate band is typical for these acids and may be used as an indicator. Since no carbohydrate structures at all were observed in the ethyl acetate extracts, it is tentatively concluded that humic or fulvic acids were not present to any significant degree.

3.5.7 Gas Chromatography/Mass Spectroscopy

Capillary-column gas chromatography/mass spectrometry (GC/MS) using a mass-sensitive detector was employed for the identification of the constituents of the ethyl acetate extracts. Two GC/MS techniques, described in more detail in Section 2.4, were applied for the analysis of these extracts. The first technique consisted of conventional, direct injection of a small amount of tetrahydrofuran (THF) solution containing the extracts. The second technique made use of a Pyroprobe insert in the interface of the GC to rapidly pyrolize the extracts at 1400°C. The resulting pyrolytic products were then analyzed following conventional GC/MS procedures.

A. Direct Injection - GC/MS

The results of the analyses of five ethyl acetate extracts (Battrum, Eyehill, Fosterton, Lone Rock and Meota) by direct injection GC/MS are tabulated in Table 19. Relative abundances were used to facilitate the reporting of the results, since the measured total abundances depended on the amount of sample injected and the sensitivity setting of the mass detector. As described in Section 2.4.11, both parameters were adjusted for each sample to achieve optimal mass spectral performance. These relative abundances were obtained by assigning the strongest peak in each chromatogram (the base peak) the arbitrary value of 100 and using the total abundances to calculate the relative values.

Because of differing response factors for each individual species, the relative abundances may not be interpreted in terms of molar composition. They can be used, however, to compare the relative composition of the five extracts and quantify any compositional changes. In order to fully obtain quantitative results, the response factors for all species must be deter-

Table 19. Composition of Ethyl/Acetate Extracts as Determined by GC/MS

Compound	Battrum	Eyehill	Fosterton	Lone Rock	Meota
	Relative Abundance[a]				
Acetic acid	10	2	50	2	nil
Propionic acid	6	5	8	4	nil
Isobutyric acid	3	6	7	nil	nil
Butyrolactone	4	nil	nil	n/a	29
Butyric acid	24	27	47	6	5
Acetophenone	nil	nil	10	nil	nil
Isovaleric acid	74	28	23	53	4
Epoxy dimethylpentane	5	nil	nil	nil	nil
Epoxy heptane	1	nil	3	nil	nil
Epoxy heptane (isomer)	nil	nil	2	nil	nil
Di-n-propylether	2	nil	nil	n/a	nil
Pentanoic (valeric) acid	9	56	94	9	16
Methylpentanoic acids	18	45	40	nil	4
Methylisopentanoate	nil	4	nil	nil	nil
Methylheptanol	nil	12	nil	nil	nil
Hexanoic acid	nil	62	85	13	15
Hexenol	nil	nil	nil	n/a	nil
Methylhexanoic acid	nil	3	6	nil	nil
Methynapthalene	1	nil	nil	nil	nil
Methylnaphthalene (isomer)	1	nil	nil	nil	nil
Benzothiazole	nil	nil	nil	nil	9
Heptanoic acid	nil	3	6	nil	nil
Phenol	8	100	90	100	52
Octanoic acid	nil	5	4	17	nil
Indanone	nil	nil	2	nil	nil
o-Ethylphenol	nil	6	nil	12	nil
m- and p-Cresols	3	55	7	57	20
o-Cresol	nil	22	9	25	9
o-Isopropylphenol	trace	2	1	5	nil
p-Ethylphenol	nil	3	nil	5	nil
m-Ethylphenol	nil	17	2	45	5
p-Isopropylphenol	nil	2	nil	19	nil
Nonanoic acid	trace	trace	4	10	5
Methylbenzofuranone	nil	nil	nil	nil	6
Dimethylphenol	nil	11	2	trace	1

Table 19 (continued)

Compound	Battrum	Eyehill	Fosterton	Lone Rock	Meota
	Relative Abundance[a]				
n-Propylphenols	nil	4	nil	nil	nil
Trimethylphenol	nil	1	nil	nil	nil
Cuminic aldehyde	nil	2	nil	trace	nil
Decanoic acid	nil	nil	trace	1	nil
Dimethylacetophenone	nil	trace	11	nil	nil
Benzoic acid	100	55	100	4	100
o-Toluic acid	8	11	19	nil	nil
p-Toluic acid	3	nil	nil	nil	6
Indandione	2	nil	1	nil	nil
Thiophene carboxylic acid	20	4	7	nil	nil
m-Toluic acid	2	17	26	nil	24
tert-Butylphenol	3	1	2	nil	2
Dimethylbenzoic acids	nil	5	3	nil	4
Chlorobenzoic acids	nil	5	nil	nil	nil
Hydroxymethylcoumarin	2	nil	nil	nil	nil
Cyanophenetole	nil	nil	nil	5	nil
Cyanophenetole (isomer)	nil	nil	nil	5	nil
Naphthoic acid	nil	nil	nil	nil	2
Ethylphenylethyl ether	nil	nil	nil	nil	4
Terpinene	nil	nil	nil	nil	4

[a] Abundance units are relative to base peaks, whose abundances are normalized at 100.

mined and the mass detector settings calibrated. Although this could be achieved by running standard compounds, time and budget constraints precluded such work.

Also, because of time constraints, GC conditions were not always perfectly optimized for polar compounds, which are known to be difficult to separate. Consequently, an overlap between peaks sometimes occurred, causing problems with the interpretation of such peaks and leading to some speculation regarding their identity. Despite these difficulties the vast majority of compounds reported in this and other sections of this report could be identified satisfactorily.

Identification of the constituents was achieved by interpretation of the fragmentation patterns of the mass spectra associated with each peak and/or by comparison with published mass spectra of authentic samples.[112] The anti-oxidant found in the tetrahydrofuran used for dissolving the extracts (2,6-di-tert-butyl-4-methylphenol) has been identified by GC/MS, but was subsequently eliminated from all results. Because of the very close similarity of the results of the GC/MS analyses of the ethyl acetate extracts and of the acidic fractions obtained by column chromatography (Section 3.7.2), the following discussion also encompasses the acidic fraction findings.

Re-emphasizing the limitations placed on the interpretation of the quantitative data (the relative abundances cannot be converted into mole fractions or concentrations without response factors), there is excellent agreement, both qualitatively (the types of compounds identified) and quantitatively (abundance ratios for compounds within each sample), between the GC/MS data on the ethyl acetate extracts and the acidic fractions. Both sets of samples consisted primarily of aliphatic carboxylic acids (ranging from acetic acid to decanoic acid), benzoic acid and substituted derivatives, and phenols. Small to trace amounts of ketones, ethers, alcohols and esters were also identified in the ethyl acetate extracts.

Most of the latter compounds were not seen in the acidic fractions, partly because some of them would probably have ended up in the neutral chromatographic fractions discussed in Section 3.7.2, and partly because the mass spectral analysis of the acidic fractions concentrated mainly on the major constituents.

In both the ethyl acetate extracts and the acidic fractions, the base peaks (the peaks with the highest abundance) were either due to benzoic acid (Battrum, Fosterton and Meota) or phenol (Eyehill and Lone Rock). The analyses also show that, in comparison, very small amounts of benzoic acid and derivatives were present in the Lone Rock samples and intermediate amounts in the Eyehill samples. On the other hand, the Battrum sample contained very small quantities of phenols, and the Meota and Fosterton samples intermediate and high amounts, respectively.

The GC/MS data on the aliphatic carboxylic acids in the ethyl acetate extracts and acidic fractions, particularly the relative abundance results of the lower molecular weight acids (C_2-C_4), appear not to agree very well. Starting with isovaleric acid, however, and extending to decanoic acid, there is generally good quantitative agreement between the two sets. The relatively low abundance of the C_2 to C_4 carboxylic acids also appear to contradict the produced water data of Table 4, which typically show declining concentrations of carboxylic acids with increasing chain lengths. At least two factors may be at work here, which could cause the low and inconsistent relative abundances of the C_2 to C_4 acids.

First, because of limited fragmentation, the total ion current (total abundance) generated by low-molecular-weight species (small molecules) is expected to be significantly smaller than that generated by high-molecular-weight species, resulting in lower response factors for smaller molecules. Second, not only is the detector signal lower for compounds such as acetic acid, but the signal was also found to be much broader causing it to partially fall below the computer threshold and thus go undetected. Hence, the combination of low response factors and signal broadening were considered responsible for the apparent inconsistencies observed. Signal optimization and calibration with standard compounds would be required to improve the accuracy.

Notwithstanding these problems, it can be concluded that aliphatic carboxylic acids from C_2 up to C_9 or C_{10} were present to varying degrees. The three fireflood samples appeared to have the highest levels, with Battrum showing no carboxylic acids above C_6, and Eyehill and Fosterton extending their responses to C_8 and C_{10}, respectively. The two steamflood samples had generally lower levels of aliphatic carboxylic acids; none were detected in the Meota sample up to C_4 or C_6. Unexpectedly, however, in the upper carboxylic acid range (C_8 to C_{10}) the Lone Rock sample contained higher levels than the Eyehill or Fosterton samples.

The only sulfur compound of significance showing up in both sets of samples is thiophene carboxylic acid. It is of interest to note that this compound is only observed in the three fireflood samples. Sulfinic or sulfonic acids, frequently speculated to be present in fireflood fluids as potent surfactants, were not detected.

Finally, ethyl acetate, the solvent used for extraction of the organic material and shown by the NMR analyses to be present in some samples, was not detected by GC/MS. The most probable reason for this is that signal detection was inhibited during a short time after injection in order to suppress the solvent signal (THF). Having a similar polarity and boiling point as THF, ethyl acetate would have a similar retention time and, hence, would be suppressed as well.

B. Analytical Pyrolysis

Although the chemical nature of high-molecular-weight constituents could not be examined directly by the use of GC/MS (temperature restrictions on the equipment employed limited analyses to volatile components with a maximum boiling range of 240-280°C), it is possible to obtain indirect information on the chemical character of these compounds by applying a technique called "analytical pyrolysis." In this procedure, the non-volatile components are subjected to a rapid increase in temperature (up to 1400°C) and the pyrolytic products so obtained are swept into the GC/MS apparatus for analysis. Since a great deal is known about the ways in which organic compounds decompose when subjected to high temperatures, an examination of the pyrolytic products provides a means for the identification of the material originally present. For example, it is known that CO_2 is produced when carboxylic acids or their esters are pyrolyzed, while CO is formed from the pyrolysis of a large variety of oxygen-containing compounds including aldehydes, ketones, phenols, alcohols and ethers. Sulfones decompose under heating with the liberation of SO_2. Consequently, if SO_2 is found in the pyrolytic products, it can be concluded that sulfones are present. Similarly, the formation of H_2S is diagnostic for the presence of sulfides, disulfides and thiols. Studies of model compounds have shown that CS_2, like CO, is much less useful diagnostically.[114] Sulfur-containing compounds such as sulfides, disulfides, sulfoxides and sulfones all produce CS_2 when pyrolyzed.

The results of the analytical pyrolysis-GC/MS analyses of the ethyl acetate extracts are shown in Table 20. Again, as in the previous section, relative abundances were used to quantify the results, since response factors were not determined and the sample quantities analyzed were not exactly the same for each sample. The identities of all the compounds listed were verified by comparison with authentic samples.

It is obvious from Table 20 that there is a striking difference between the results from the fireflood and the steamflood samples. The most abundant peak in the former is due to benzene, while in the latter it is due to CO. These findings are compatible with the GC/MS results from the direct injection analyses. Benzene is the major pyrolytic product of

Table 20. Major Products Obtained from Analytical Pyrolysis of Ethyl Acetate Extracts, as Determined by GC/MS

Compound	Battrum	Eyehill[b]	Fosterton	Lone Rock	Meota
	Relative Abundance[a]				
Carbon Monoxide	40	47	34	100	100
Carbon Dioxide	39	23	26	39	57
Hydrogen Sulphide	nil	nil	nil	2	nil
Hydrogen Cyanide	nil	nil	nil	4	5
Carbon Disulfide	8	37	6	8	9
Benzene	100	100	100	46	77
Thiophene	1	nil	1	nil	nil
Toluene	31	41	32	24	57
Ethylbenzene	3	4	3	3	7
Styrene	8	3	5	5	8
Indene	10	3	trace	10	9
Naphthalene	20	6	3	15	10

[a] Abundance units are relative to base peaks, whose abundances are normalized at 100.

[b] A trace amount of SO_2 was detected.

benzoic acid. Previous work by Lee, Noureldin and Mourits[114] shows that benzoic acid is primarily pyrolyzed to benzene (100), CO_2 (18), and toluene (5).* These products are all present in significant quantities in the pyrolyzed fireflood samples, thus confirming the presence of high levels of benzoic acids. The excess CO_2 would be due to carboxylic acids (or esters), while the considerable CO levels are in agreement with the presence of phenols.

Although less diagnostic, the high CO levels in the pyrolyzed steamflood samples are, given the previous GC/MS analyses, undoubtedly due to phenols. In the same work just cited, a 2-tert-butyl-4-methylphenol was pyrolyzed and produced CO (100), acetylene (40) and diacetylene (27).* The pyrolyzed Meota sample also contained substantial amounts of benzene, CO_2 and toluene, which again confirms the presence of benzoic acids in the original sample. The apparent excess of CO_2 is in agreement with the presence of carboxylic acids. The Lone Rock sample, in comparison, produced the lowest levels of benzene and toluene, and therefore contained the least amount of benzoic acids. Its CO_2 production was not proportionally lower, however, indicating the presence of other CO_2-producing compounds such as carboxylic acids.

As remarked above, the presence of CS_2 does not have any diagnostic value other than as an indicator of the presence of sulfur-containing compounds in the original sample. In this sense, the high CS_2 level in the pyrolyzed Eyehill sample is unexpected. Unfortunately, a sulphur elemental analysis on the Eyehill extract (see Table 9) is not available to confirm a possibly higher than average sulfur content. The detection of thiophene in the pyrolyzed Battrum and Fosterton samples, although occurring in trace amounts, is in agreement with the previously confirmed presence of thiophene carboxylic acid in the original extracts.

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*The figures in parentheses are relative abundances.

3.6 CHARACTERIZATION OF AQUEOUS PHASES AFTER EXTRACTION

After the acidified permeates were extracted with ethyl acetate and the ethyl acetate layer was removed, an aqueous layer presumably depleted of dissolved organic material remained. In order to determine how effective the extraction step had been in removing the organics, the remaining water phase was examined for organic material.

At first, it was attempted to perform total organic carbon (TOC) analyses on the water phases, but this approach was abandoned after unusually high readings were obtained. It was concluded that these high TOC values were due to the high solubility of ethyl acetate in water. As an alternative approach, the aqueous layers were evaporated to dryness using rota-evaporation, a process that also removed the ethyl acetate. The dried residues so obtained were then subjected to elemental analysis. Although of interest for comparative purposes only, the yields of the dried residues were recorded and listed in Table 8.

3.6.1 Elemental Analysis

The elemental analyses (C, H and N only) of the residues obtained by drying the aqueous phases after extraction are given in Table 21. In order to determine the extraction efficiency, these results should be compared to the elemental analyses of the dried raw permeates (Table 9). If the same weight basis was to be used, the carbon extraction efficiencies would vary from a high of 95.9% (Eyehill) to a low of 73.9% (Meota). The actual figures could, however, be slightly lower because the weight basis may have changed due to the addition of inorganic material (acidification). Any increase in the amount of dissolved inorganic material should be evident from the yields of the dried residues (Table 8), but volume changes due to ethyl acetate dissolution and possibly incomplete drying, as suggested by the relatively high hydrogen contents of some of the residues (Table 21), caused inconclusive variations in the yields.

Table 21. Elemental Analysis of Aqueous Phase Residues[†]

	Elemental Analysis (Wt %)		
	C	H	N
Battrum	0.57	0.87	0.03
Eyehill	0.7	3.7	0.04
Fosterton	1.8	2.4	0.07
Lone Rock			
Unaged	-	-	-
1 Week	-	-	-
1 Month	0.26	0.20	0.01
Meota	0.48	0.36	0.02

[†] After extraction of organic materials with ethyl acetate.

3.7 CHROMATOGRAPHIC FRACTIONS

Following the procedures outlined in Section 2.3.3, the five raw permeates were acidified to pH 2 and passed through a polystyrene-divinylbenzene resin-packed chromatographic column, which adsorbed the organic materials in the permeates. By subsequently eluting these materials with base, acid and methanol, acidic (A), basic (B_1) and neutral (N_1) fractions were obtained. Repeating this procedure with the effluent from the first pass through the column (after adjusting the pH of the effluent to 12 and only using acid and methanol eluents) produced additional basic (B_2) and neutral (N_2) fractions (see Figure 5). These secondary adsorption/elution steps were performed to increase the recovery efficiency of the basic and neutral compounds in the permeates.

As a result of this separation scheme, a total of 25 sample fractions were obtained. Their appearance (see Table 22) varied from dark yellow for most of the acidic and primary neutral (N_1) fractions to pale yellow/green for the secondary neutral (N_2) fractions, or essentially clear for all the basic fractions. Before these fractions were subjected to infrared and GC/MS analysis, the results of which will be discussed in the following sections, their respective pH values were adjusted to convert any organic acids and bases present to their non-ionized (neutral) forms. Thus, the pH of the acidic fractions was lowered to 5 and the pH of the basic fractions raised to 8. As shown in Table 22, precipitates formed after pH adjustment, especially in the basic fractions of the fireflood samples (iron hydroxides). The acid steamflood fractions, in agreement with previous observations, produced brown precipitates on acidification.

Since infrared analyses can only be performed on water-free samples, further workup of the fractions was required. Details of the drying and organics extraction steps were given in Section 2.3.3.

Table 22. Appearance of Chromatographic Fractions Before and After pH Adjustment

Fraction	Battrum	Eyehill	Fosteron	Lone Rock	Meota
	As Eluted				
A	Dark Yellow ppt	Yellow	Dark Yellow ppt	Amber	Dark Yellow
B_1	Clear	Clear	Clear	Clear	Clear
N_1	Yellow	Yellow	Yellow	Dark Yellow	Dark Yellow
B_2	Clear	Pale Green	Clear	Pale Green	Clear
N_2	Very Pale Yellow	Pale Green	Pale Yellow	Pale Green	Pale Yellow
	After pH Adjustment				
A	Yellow	Pale Yellow	Pale Purple Brown ppt	Yellow Heavy brown ppt	Pale Yellow Brown ppt
B_1	Clear Yellow/Brown ppt	Clear	Clear Yellow/Brown ppt	Clear	Clear
N_1	Pale Yellow	Pale Yellow	Pale Yellow	Dark Yellow	Yellow
B_2	Clear White White ppt	Clear Heavy brown ppt	Clear Yellow/Brown	Clear Brown ppt	Clear
N_2	Clear	Clear	Clear	Very Pale Yellow	Very Pale Yellow

An attempt was also made to perform ^{13}C NMR analysis on the chromatographic samples. Overnight runs using 200 MHz and 300 MHz NMR spectrometers revealed some small peaks (Battrum A fraction) or no signals at all (Lone Rock N_1 fraction). These two fractions were selected because their dark yellow colour suggested sufficiently high concentrations of dissolved organic materials. Obviously, this was not the case. The poor results from the overnight runs therefore, did not warrant further NMR work on other chromatographic samples.

3.7.1 Infrared Analysis

A. Acidic Fractions

The infrared spectral data on all five acidic fractions obtained by column chromatography are listed in Table 23.

a) Presence of Solvent

Because of the presence of absorption bands at 3650-2930 cm^{-1}, 1750-1580 cm^{-1} and below 930 cm^{-1}, the presence of water cannot entirely be ruled out. The band at 1600 cm^{-1} in the spectra of the acidic fractions is slightly shifted relative to the blank spectrum of a KCl pellet with water added (1640 cm^{-1}). Thus, water may be present albeit in small amounts.

b) Functional Groups

The IR spectra of the acidic fractions are similar, but slightly broader than the spectra of the ethyl acetate extracts, indicating the possibility of a greater variety of compounds present in the acidic chromatographic fractions. The spectra of the individual samples are again very similar and will, therefore, be discussed simultaneously.

Table 23. Infrared Absorption Data of Acidic Fractions from Chromatography

Wavenumber (cm^{-1})						
Firefloods			Steamfloods		Blank KCl Pellet With Water Added	
Battrum	Eyehill	Fosterton	Lone Rock	Meota		Vibrational Mode
3100	3400	3400	3300	3340	3400	- Carboxylic acid O-H stretch; phenol or alcohol O-H stretch; H_2O
2950	2960,2930	2960,2930	2950	2960,2930		- C-H stretch
2600 sh	2640 sh		2640 sh	2640 sh		- Thio-compounds S-H stretch
1920						- Unassigned
1700	1700	1750 sh	1705	1705		- Carboxylic acid C=O stretch
					1670,1640	- H_2O
1600	1600	1560	1610	1620		- Carboxylic acid anion C=O stretch; aromatic skeletal vibrations; olefin C=C stretch
1400	1410	1410	1440	1410		- Carboxylic acid COH in-plane bending; carboxylic acid anion CO_2 symmetric stretch; carbonate ion CO asymmetric stretch; C-H bending
1250	1280	1300				- Carboxylic acid dimer CO stretch
1150		1140	1160	1170	1160	- H_2O
1050	1050		1080 sh	1080		- Phenol or alcohol C-O stretch; aromatic ring C-H bending
	950		950	950		- Carboxylic acid OH out-of-plane bending
		840	815			- Unassigned
765	760	760	760	790		- Unassigned
715	730	715				- Unassigned
630	655	620	650	610		- Unassigned
530		520				- Unassigned
		470		460	470	- H_2O

sh = shoulder

The broad bands between 3400-3100 cm^{-1} are attributed to O-H stretching vibrations from both carboxylic acids and phenols. The presence of carboxylic acids is supported by the C=O stretch at 1705-1700 cm^{-1} and the bands at 1440-1400 cm^{-1}, 1300-1250 cm^{-1} and 950 cm^{-1}. Carboxylic acid anions are also present, as indicated by the bands at 1620-1600 cm^{-1} and 1440-1400 cm^{-1}.

The literature search on the chemical nature of surfactants as determined by infrared spectroscopy uncovered several papers of interest. A report from Zenon identified the isolated acid fraction of a bitumen emulsion as naphthenic acids.[2] Isaacs and Morrison published an infrared spectrum of interfacial film material that developed photolytically between bitumen and water surfaces.[16] They identified "petroacids" as being responsible for the spectrum. The spectra published by both Zenon,[2] and Isaacs and Morrison[16] are very similar to the spectra of the acidic chromatographic fractions in this study. Differences between the latter spectra and the spectra in the literature cited include a more broadened appearance of the bands in the spectra recorded here as well as the presence of a higher intensity band at 1600 cm^{-1}. A 1600 cm^{-1} band was not present in the spectrum of Zenon's naphthenic acid standard, while it appeared as a shoulder in their sample spectrum.

Consideration of an infrared study on emulsion surfactants published by Baptista and Bowman is germane to our study.[63] These investigators isolated surfactant material from Athabasca oil sands by foam fractionation and then acidified this waxy material. The original waxy material before acidification produced an infrared spectrum with the C=O stretching band appearing at 1600 cm^{-1}, indicative of carboxylic acid anions, a feature exhibited in the spectra of the acidic fractions isolated in this study. When Baptista and Bowman acidified the original waxy material, the resulting infrared spectrum displaced a shift of the 1600 cm^{-1} band to 1700 cm^{-1}. The latter spectrum was basically the same as those obtained by Zenon[2] and by Isaacs and Morrison.[16]

In summary, the spectra of the acidic chromatographic fractions from this study are very similar to the spectra from Zenon,[2] Isaacs and Morrison[16] and the acidified material from Baptista and Bowman.[63] The present spectra, however, contained a more intense band at 1600 cm^{-1}, exactly as shown by the carboxylic acid anionic material from Baptista and Bowman.[63] This suggests that the acidic materials were not wholly returned to their nonionic forms.

Turning to other bands, phenols are indicated by the 3400-3100 cm^{-1} band (O-H stretch) and by the 1080-1050 cm^{-1} band (C-O stretch). Carbonate ions may again be present, judging by the 1440-1400 cm^{-1} and 840-815 cm^{-1} bands present in the Fosterton and Lone Rock samples. Thio-compounds are also again indicated by the 2640-2600 cm^{-1} shoulders present in all spectra but Fosterton.

c) Spectral Differences Between Individual Samples

One of the most obvious differences is found in the spectrum of the Battrum sample. A broad O-H stretching band occurs at 3100 cm^{-1}, a much lower frequency than found for this band in the spectra of the other samples (3400-3300 cm^{-1}). This lower value is more typical of carboxylic acids than of phenols. Thus, it was concluded that the Battrum sample had a lower ratio of phenols to carboxylic acids than the other samples. This is in agreement with the ^{13}C NMR and the GC/MS results.

Another significant difference occurs in the Fosterton spectrum. This spectrum shows the carboxylic acid C=O stretching band at 1700 cm^{-1} as merely a shoulder on the much more intense carboxylic acid anion C=O stretching band at 1600 cm^{-1}, indicating a much larger proportion of acids existing in their anionic state. This is in contrast to the other samples, where the proportion of acids in their anionic forms was small. Assuming that all samples were isolated and prepared for infrared spectroscopy in the same way, including lowering of the pH of the acidic fractions to the same values (pH 5-6), a possible reason could be that the Fosterton carboxylic acids had a lower pK_a than those in the other samples.

B. Neutral Fractions

Infrared spectral data on all five primary neutral (N_1) fractions and one secondary neutral fraction (Eyehill N_2) are listed in Table 24.

a) Presence of Solvent

The major absorption bands for the solvent (methanol) are tabulated in Table 23. Using the strong 1030 cm^{-1} band as an indicator of the presence of methanol, very little solvent is concluded to be present.

b) Functional Groups

The neutral fractions isolated by column chromatography were obtained by two pathways, yielding primary N_1 fractions and secondary N_2 fractions (see separation scheme, Figure 5). The infrared spectra of the N_2 fractions were found to be essentially low-concentration duplicates of the respective N_1 spectra, and so they will not be discussed separately. An exception was the Eyehill N_2 spectrum, which was very similar to the other N_2 spectra, but did not match its N_1 counterpart.

The spectra of three neutral N_1 fractions closely resemble the spectra of the acidic fractions (Lone Rock, Meota) or can be considered a low-intensity version of the corresponding acidic fraction spectrum (Battrum). Thus, the same compounds as those identified in the discussion of the spectra of the acidic fractions are found here, although possibly in lower concentrations. The Eyehill and Fosterton spectra, on the other hand, are considerably different from their acidic fraction counterparts. These differences pertain primarily to the position of the carbonyl (C=O) stretch band in the 1700-1600 cm^{-1} region and the intensity of the 1400 cm^{-1} carboxylic acid/carboxylic acid anion band.

Table 24. Infrared Absorption Data of Neutral Fractions from Chromatography

Wavenumber (cm^{-1})							
Firefloods				Steamfloods			
Battrum N_1	Eyehill N_1	Eyehill N_2	Fosterton N_1	Lone Rock N_1	Meota N_1	Methanol	Vibrational Mode
3420	3400,3150	3400	3200	3300	3250	3360	- Carboxylic acid O-H stretch; phenol or alcohol O-H stretch; methanol
2950	3020	2960,2930 2870	2970,2930 2870	2950,2930 2870	2950,2930 2870	2940,2830	- C-H stretch; methanol
			2600 sh	2600 sh	2560 sh		- Thiocompounds S-H stretch
1720		1715	1760,1715	1720	1715		- Carboxylic acid C=O stretch
1620	1635	1650	1610	1640,1610	1640,1610		- Carboxylic acid anion C=O stretch; aromatic skeletal vibrations; olefin C=C stretch
1420	1405	1450,1405	1450,1405	1440	1450	1450,1410	- Carboxylic acid COH in-plane bending; carboxylic acid anion CO_2 symmetric stretch; carbonate ion CO asymmetric stretch; C-H bending; methanol
			1380	1380	1380		- C-H bending
1280,1210		1195	1290	1280,1210	1270,1210		- Carboxylic acid dimer CO stretch
			1115			1110	- Methanol
	1060,1015	1070,1045	1040		1040	1030	- Phenol or alcohol C-O stretch; aromatic ring C-H bending; methanol
		940					- Carboxylic acid OH out-of-plane bending
815					840		- Unassigned
			760	760	760		- Unassigned
			700				- C-H bending

In the Eyehill case, the carbonyl stretch band shifted from 1700 cm^{-1} in the acidic sample spectrum to 1635 cm^{-1} in the N_1 spectrum, while the intensity of the band at 1400 cm^{-1} sharply increased and the carboxylic acid dimer C=O stretch band at around 1280-1250 cm^{-1} completely disappeared. These changes would indicate the presence of only carboxylic acid anions in the Eyehill N_1 fraction as compared to mostly carboxylic acids in the acidic fraction. Carboxylic acid anions were definitely not expected in the neutral fraction. Surprisingly, the Eyehill N_2 spectrum displays a much reduced presence of carboxylic acid anions and, consequently, is much closer in appearance to the spectra of the other neutral samples.

The Fosterton N_1 spectrum is evidence that just the opposite of what was found in the Eyehill case occurred. The single carboxylic acid anion band at 1560 cm^{-1} in the acid spectrum shifted upwards to 1715 cm^{-1} in the N_1 spectrum, while leaving a shoulder at 1610 cm^{-1}. The strong band at 1400 cm^{-1} in the acid spectrum was reduced in intensity and split, while a new, broad band appeared around 1300-1200 cm^{-1}. These changes point to the presence of primarily carboxylic acids in the Fosterton N_1 sample, as opposed to mostly carboxylic acid anions in the Fosterton acidic fraction. The general appearance of the Fosterton N_1 spectrum is very similar to the Battrum, Lone Rock and Meota spectra.

Thiocompounds are indicated in the spectra of Fosterton, Lone Rock and Meota samples. In the other samples, they may occur in concentrations too low to appear in the infrared spectra.

The finding of carboxylic acids or their anions in these neutral fractions leads to two conclusions: i) the separation into acidic and neutral fractions was not completely successful; and ii) the presumably lower concentrations of acidic compounds eluted as part of the neutral fractions absorbed more strongly in the infrared spectral region than all of the neutral compounds in these fractions.

c) Spectral Differences Between Individual Samples

As described above, the Eyehill N_1 spectrum was very different from the other N_1 spectra because of the presence of carboxylic acid anions. The Eyehill N_2 spectrum, although more difficult to compare due to the low N_2 sample concentration, was similar to the other N_2 samples.

C. Basic Fractions

Infrared spectral data on all five primary basic (B_1) fractions and one secondary basic fraction (Battrum B_2) are listed in Table 25.

a) Presence of Solvent/Functional Groups

The basic fractions resulting from the column chromatographic separation were obtained by two pathways, yielding primary B_1 fractions and secondary B_2 fractions (see separation scheme, Figure 5). With the exception of the Battrum B_2 fraction, the B_2 fractions were all essentially identical to their B_1 counterparts.

All spectra exhibit weak absorbances at around 3400, 1640, 1610 and 620 cm^{-1}. These bands are identical to those seen in the spectrum of a KCl disk with water added. Thus, traces of water were present in all samples. No other features are present in the two steamflood samples. In the spectra of the three B_1 fireflood samples, the 3400 cm^{-1} band is less broad, showing four distinct peaks at 3540, 3480, 3420 and 3240 cm^{-1}. Otherwise no other features are present except for the water absorption bands. The fine structure on the 3400 cm^{-1} band is possible due to amines or amine salts.

b) Battrum B_2 Fraction

The spectrum of the Battrum B_2 fraction is intense and completely dif-

Table 25. Infrared Absorption Data of Basic Fractions from Chromatography

Wavenumber (cm^{-1})							
Firefloods				Steamfloods			
Battrum B_1	Battrum B_2	Eyehill B_1	Fosterton B_1	Lone Rock B1	Meota B1	Blank KCl Pellet With Water Added	Vibrational Mode
3540,3480	3400	3540,3480	3540,3480	3440	3430	3400	- H_2O; N-H stretch for fine detail (3540, 3480, 3420 cm^{-1})
3420		3410	3420				
3240		3240	3240				- Unassigned
	2220						- Unassigned
1640,1620	1635	1640	1640,1610	1640	1640	1670,1640	- H_2O
	1555						- Unassigned
	1460						- Unassigned
1440			1420				- Unassigned
	1405						- Unassigned
						1160	- H_2O
1015	1015						- Unassigned
620		600	620			640	- H_2O

ferent from its B_1 counterpart. The 3400 cm^{-1} band is very broad and intense, and there are also intense peaks at 1635 and 1405 cm^{-1}. Water could be present, but it would not account for the 1405 cm^{-1} band and a smaller band at 1550 cm^{-1}. The latter two absorbances suggest the possible presence of carboxylic acids (1635 cm^{-1}) and carboxylic acid anions (1550 cm^{-1}), which would again be the consequence of incomplete separation.

Finally, there is a broad absorption band around 2200 cm^{-1}. Bands seldom appear in the region 2260-2100 cm^{-1}, but if they do, they usually indicate the presence of triple bonds. Triple bonds are, however, not normally encountered in organic materials from petroleum reservoirs. Also, if they were present, it would be unlikely that the absorption band at 2200 cm^{-1} would be as broad as the one observed here at 2220 cm^{-1}.

3.7.2 Gas Chromatography/Mass Spectroscopy

Capillary column gas chromatography/mass spectroscopy using a mass-sensitive detector was employed for the identification of the constituents in the chromatographic fractions. In order to be able to analyze these aqueous fractions directly, without additional extraction steps with organic solvents, a sample concentrator was used in conjunction with the GC/MS equipment. This device can remove such solvents as water or methanol, which in large quantities have a damaging effect on both the GC column and the mass detector. At the same time, by removing the solvent the dissolved organic materials are concentrated and can more easily be detected. This technique was, therefore, quite suited for the analysis of the various chromatographic fractions, some of which were expected to have relatively low concentrations of organic materials.

Further details on the sample concentrator and operational procedures are provided in Section 2.4.11. As described, the concentration was designed to extract only volatile compounds. In order to include compounds with higher boiling points as well, compromised procedures were followed, which eventually led to damage to the GC column and a sharply reduced sensitivity of the mass detector. It is not known, if or how this reduced sensitivity has affected the following results.

A very similar study was reported in 1981 by the Argonne National Laboratory (ANL), using a Hewlett-Packard GC/MS to analyze the acid, base and neutral fractions of liquid filtrate and particulate-phase methylene chloride extracts of raw process water samples, collected from two tar sands oil recovery experiments (combustion and steam injection).[118] As will be discussed below, there is generally a very satisfactory qualitative agreement between the ANL study and this work, especially where the acid and neutral fractions are concerned.

A. Acidic Fractions

The results of the GC/MS analyses of all five acidic fractions obtained by column chromatography are tabulated in Table 26. As was the case with the GC/MS data on the ethyl acetate extracts (Section 3.5.7), relative abundances were used--in the absence of response factors--to quantify the results and provide a means to compare sample compositions.

Given the different sample workup procedures followed, the results in Table 26 are in remarkably close agreement with the GC/MS data on the ethyl acetate extracts. For this reason the two sets of results were discussed together in Section 3.5.7. There is also good agreement with the above-cited ANL study, which found a mixture of 40% carboxylic acids (C_3-C_9), 50% phenols (C_0-C_2) and 5% lactones (identified in the ethyl acetate extracts, see Table 19) in the combustion samples, and exclusively (i.e. 100%) phenols (C_0-C_3) in the steam injection sample.[118] No benzoic acids were found in this study, however.

Table 26. Composition of Acidic Fractions from Chromatography as Determined by GC/MS

Compound	Battrum	Eyehill	Fosterton	Lone Rock	Meota
	Relative Abundance[a]				
Acetic acid	4	2	30	25	nil
Propionic acid	1	1	3	5	nil
Isobutyric acid	1	3	nil	8	nil
Butyric acid	15	4	5	23	trace
Isovaleric acid	30	13	10	27	trace
Pentanoic (valeric) acid	2	7	31	trace	8
Methylpentanoic acid	12	15	60	trace	trace
Hexanoic acid	16	12	90	7	10
Methylhexanoic acid	trace	1	10	trace	trace
Heptanoic acid	3	39	90	13	trace
Phenol	2	100	60	100	39
Octanoic acid	nil	1	10	16	nil
o-Ethylphenol	nil	16	nil	20	nil
m- and p-Cresol	nil	56	trace	80	10
o-Cresol	nil	26	trace	40	2
o-Isopropylphenol	nil	trace	trace	13	nil
p-Ethylphenol	nil	trace	trace	12	nil
Nonanoic acid	nil	nil	10	12	2
p-Isopropylphenol	nil	3	nil	29	trace
m-Ethylphenol	nil	15	nil	67	trace
Dimethylphenols	12	34	nil	7	trace
Decanoic acid	nil	nil	5	4	nil
Benzoic acid	100	29	100	3	100
o-Toluic acids	13	12	70	nil	22
Thiophene carboxylic acid	nil	nil	3	nil	nil
tert-Butylphenol	trace	trace	trace	trace	10
Dimethylbenzoic acid	8	trace	20	nil	trace
Chlorobenzoic acids	trace	trace	trace	nil	nil
Trimethylbenzoic acids	3	nil	5	nil	nil
Isopropylbenzoic acid	2	trace	2	nil	nil
Butylmethoxyphenol	2	trace	nil	nil	nil

[a] Abundance units are relative to base peaks, whose abundances are normalized at 100.

B. Neutral Fractions

The results of the GC/MS analyses of the primary Battrum (N_1) and Lone Rock (N_1) neutral fractions are tabulated in Tables 27 and 28, respectively. More than 60 compounds could be identified in the Battrum sample and, as expected, these compounds were mainly ketones and esters. Some hydrocarbons, aldehydes, amines and heterocyclics were identified as well.

Over 40 compounds were identified in the neutral (N_1) Lone Rock sample. Surprisingly, phenols comprised a significant proportion of these compounds, which would point to poor chromatographic separation. Alcohols and phenols were also found in the neutral combustion sample analyzed by ANL.[113] The main compounds in the ANL neutral combustion sample were lactones and ketones, whereas in the ANL neutral steamflood sample cyclohexanes or alkenes were the most prevalent.

C. Basic Fractions

Two primary basic fractions (Battrum B_1 and Lone Rock B_1) were investigated by GC/MS, but no peaks could be detected. This was most likely due to very low or non-existent concentrations of basic compounds. Deterioration of the mass detector sensitivity may also have been a factor in these negative results.

Table 27. Composition of Battrum Neutral Fraction from Chromatography as Determined by GC/MS

Compound	Battrum N_1 Relative Abundance[a]
Methylallyl ketone	2
1,2-Dimethylene cyclobutane	8
Methylacetate	2
Tetrahydropyran	3
Cyclopropylmethyl ketone/ methylpropenyl ketone	1
Propylene glycol	32
2-Methyl-1,3-dioxalane	1
Ethylacetoacetate	1
2-Methyl-4,5-dihydrofuran	3
Toluene	1
Methylcyclohexene	4
2-Octanol	2
Isobutylhydroxylamine	1
2-Furylmethyl ketone	1
Guanidine	8
U.I.C.[b]	13
2-Pentanone	1
Trimethylamine	3
Methylcyclopentanone	8
Hexenal	1
methylpentanone	1
o-Xylene	6
m- and p-Xylenes	10
3-Methyl-2-thiapentane	6
Heptanone	4
Cyclooctatetraene	1
Vinyl butyrate	19
U.I.C.	18
2-Cyclohexanone	5
Isopropylbenzene	1
Cyclooctane	4
methylcyclohexanone	1
U.I.C.	7
U.I.C.	4
Dimethylhexane	13
Dimethylhexane (isomer)	18
Dimethylhexane (isomer)	36
Dimethylmalononitrile	11
Isoamyl acetate/Dimethylpropyl acetate	23
U.I.C.	12
U.I.C.	24
U.I.C.	38

(continued)

Table 27 (continued)

Compound	Battrum N_1 Relative Abundance[a]
Bromomethylbutane	54
Trimethylbenzene	10
U.I.C.	22
1-Methylpyrrole	100
Methylbenzoate	27
U.I.C.	7
2-Decanone	6
Decylaldehyde	3
Dimethylbenzaldehyde	6
U.I.C.	9
Methylphenylacetate	9
Methylacetophenone	14
Methylhexanoate	9
Tetramethyltetrahydrofuran	13
U.I.C.	19
U.I.C.	15
U.I.C.	13
U.I.C.	24
U.I.C.	11
U.I.C.	17
U.I.C.	15
U.I.C.	12
tert-Butylacetate	24
U.I.C.	12
U.I.C.	15
2,5-Dimethyl methylbenzoate	17
2,4-Dimethyl methylbenzoate	24
3,5-Dimethyl methylbenzoate	5
2,3-Dimethyl methylbenzoate	9
Ethylmethylbenzoate	12
4-Decanone	1
Heptalactone	5
Butylbenzene	1
Naphthalene	2
Methyltoluate	2
Ethylhexylacetate	2
Ionone	4
Di-tert-butylpyrazine	3
Isopropylidenehydrazino thiophene	1
Dimethylphenanthrene/ethylphenanthrene	3

[a] Abundance units are relative to base peak, whose abundance is normalized at 100.

[b] U.I.C.: Unidentified compound.

Table 28. Composition of Lone Rock Neutral Fraction from Chromatography as Determined by GC/MS

Compound	Lone Rock N, Relative Abundance[a]
Methylpentanone	1
Dimethylcyclohexene	1
Dimethylcyclohexene (isomer)	1
Methylenemethylcyclohexene	2
Methylenemethylcyclohexene (isomer)	4
Methylenemethylcyclohexene (isomer)	9
Cresol	7
Methylindan	2
Methylindan (isomer)	1
2,3-Dimethylphenol	1
o-Ethylphenol	14
3,4-Dimethylphenol	20
m-Ethylphenol	94
2,4-Dimethylphenol	6
Benzoic acid	3
m-Ethylphenol (isomer)	17
2,4,5-Trimethylphenol	4
n-Propylphenol	7
o-Isopropylphenol	31
m-Isopropylphenol	27
p-Isopropylphenol	4
n-Propylphenol (isomer)	65
2,3,5-Trimethylphenol	12
Ethylmethylphenol	10
3,4,5-Trimethylphenol	4
Thymol	8
Diethylphenol	8
Ethylbenzaldehyde	33
Dimethylbenzaldehyde	3
Dimethylbenzaldehyde (isomer)	100
Methyl-tert-butylbenzene	16
tert-Butyltoluene	11
Ethylcumene	36
Diisopropylbenzene	2
Diisopropylbenzene (isomer)	1
Diisopropylbenzene (isomer)	1
Ethylcumene (isomer)	1
Anthracene/Phenanthrene	3
Cinnamaldehyde	12
Allylbenzimidazole	39
Allylbenzimidazole (isomer)	28

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[a] Abundance units are relative to base peak, whose abundances are normalized at 100.

4. SUMMARY AND CONCLUSIONS

SAMPLE COLLECTION AND PREPARATION

Wellhead emulsions were collected from two steamflood projects (Texaco Lone Rock and Canterra Meota) and three fireflood projects (Mobil Battrum, Murphy Eyehill and Mobil Fosterton N.W.). The selection of the steamflood samples was based on the presence of oil-in-water emulsions in the produced water. The oil concentration in the water phase ranged from 0.4 mg/L for the Lone Rock sample to an average of 4.5 mg/L for the Meota sample. Total organic carbon (TOC) levels of the oil-free water phases varied from 30-110 mg/L. The fireflood emulsions were selected on the basis of treatability: only difficult-to-break (i.e. tight) water-in-oil emulsions were chosen. Their water content (BS&W) varied from 10% v/v (Eyehill) to 76% v/v (Fosterton). Essentially no free (produced) water was present in the Eyehill and Fosterton samples.

Since ultrafiltration as a technique to separate surfactants had previously only been applied to low-concentration oil-in-water emulsions, a method was developed to prepare the fireflood emulsions for membrane permeation. The produced-water-free Eyehill and Fosterton emulsions were vigorously stirred with added water. This caused the partial formation of unstable oil-in-water emulsions that broke quickly. The washing action extracted substantial amounts of water-soluble organic materials as shown by subsequent TOC analyses (150-1133 mg/L) on the free water phases. A similar wash of the Battrum emulsion with its own produced water did not measurably raise the already high TOC level (1110 mg/L) of the water phase. After the oil/water mixtures had completely separated, the water phases were removed from the oil and stored in separate containers, in readiness for permeation.

ULTRAFILTRATION

When ultrafiltration of fresh Meota sample was attempted using the originally recommended Polysulfone E500 membrane (pore size 0.04 µm), low (1 m^3/m^2.day) to zero permeation rates were obtained. Earlier test runs on seven-month old (and likely oxidized) Meota oil-in-water emulsions had provided acceptable permeate flux rates (2-19 m^3/m^2.day) and had not pointed to any potential problems. In an attempt to improve ultrafiltration performance, various possible causes were identified and investigated, including membrane type and supplier, membrane fouling, plugging of the permeation cell, sample oxidation and operating temperature. Generally confusing results were obtained and no one single factor could be identified. It appeared, however, that a combination of exposure to air, pumping and circulation of the emulsion, and long settling times minimized membrane fouling and resulted in good permeation rates. This would explain the success of the runs using aged emulsions.

The highest, longest-lasting permeation rates with fresh emulsions (16.5 m^3/m^2.day, declining to 3 m^3/m^2.day over 7 hours) were achieved using a Nylon-66 0.2 µm membrane, a permeation cell with the sintered plate cleaned before each run and skimmed (free oil removed) emulsion. Other membranes tested (Cellulose Nitrate 0.01 µm and Nylon-66 0.1 µm) performed worse or only slightly better than the Polysulfone E500 membrane.

Although the above results already answer some of the questions regarding the aging of emulsions, further research in this area was done by allowing fresh Lone Rock samples (stored in air-free containers) to age for one day, one week and one month, respectively, before permeation was performed and the permeate products analyzed. No differences were found as far as permeation was concerned. The characterization results of these three samples are summarized below.

SURFACTANT ISOLATION AND CHARACTERIZATION

The originally proposed separation scheme called for three isolation methods. Following the first method, portions of the raw permeates were evaporated to dryness through freeze-drying or rota-evaporation. The mixed organic/inorganic residues thus obtained were then analyzed by elemental analysis and infrared spectroscopy.

The second method consisted of acidification of the raw permeates. The precipitates expected to be so formed would constitute the main organic product in this study and, hence, were to be characterized by a wide array of analytical methods. However, only the two steamflood samples formed precipitates and then only in very small quantities. Because of the failure to obtain sufficient quantities of organic material by precipitation, direct extraction of the acidified permeate with ethyl acetate instead of extraction of the supernate (original scheme) was performed on all five samples. The organic extracts so obtained (after removal of the solvent yields varied from 50-600 mg/L) were subjected to extensive characterization, including elemental analysis, vapour phase osmometry (molecular weight determination), acid number determination, thermal gravimetric analysis, infrared spectroscopy, ^{13}C NMR and GC/MS.

The third method consisted of separation of the raw permeates by column chromatography. The original reverse-phase chromatography method, only capable of separating the organics from the inorganics, was replaced by a scheme which further separates the organics into acidic, neutral and basic fractions. It was reasoned that analyses performed on these separated fractions would be more meaningful and easier to interpret than when a whole organic fraction would be subjected to analysis. Infrared spectroscopy and GC/MS were used for characterization of the chromatographic fractions. ^{13}C NMR spectroscopy has been attempted, but the sample concentrations were too low, even for overnight runs.

COMPARISON OF CHARACTERIZATION RESULTS

a) Lone Rock Aging Study

The infrared spectra of the three Lone Rock samples aged one day, one week and one month, respectively, were virtually the same for all fractions examined (i.e. the dried residues from the raw permeates, the precipitates from acidification and the ethyl acetate extracts), although some intensity differences in bands occurred, due to pellet thickness differences. It was, therefore, concluded that no effects of sample aging were detectable as far as permeation performance (see above) or infrared analysis were concerned.

After this conclusion was reached, all remaining analyses, unless specified otherwise, were performed only on the fresh (aged one day) Lone Rock samples.

b) Battrum and Fosterton Samples

Perhaps not surprisingly, the organic matter extracted from the Battrum and Fosterton fireflood emulsions, both originating from the same formation (Roseray Sand) and both produced by in-situ wet combustion, exhibited many similarities. The elemental analyses of the dried permeates and ethyl acetate extracts showed that their C/H ratios were the highest (the ethyl acetate extract values were 0.84 for Battrum and 0.83 for Fosterton) among the four samples analyzed. This would indicate a higher aromatic character than the Eyehill and Lone rock samples. The ^{13}C NMR and GC/MS results are in good agreement with this finding. Based on the NMR data, the molar composition of the Battrum ethyl acetate extract was estimated to be 72% benzoic acids, 6% phenols and 22% aliphatic carboxylic acids. The molar composition of the Fosterton ethyl acetate extract was estimated at 37% benzoic acids, 5% phenols and 59% aliphatic carboxylic acids. Although the non-quantitative GC/MS data only permit inter-sample comparison of abundance ratios of compounds in a sample, this information is sufficient to confirm that the Battrum ethyl acetate extract and the Battrum acidic chromatographic fraction had, in comparison, the highest concentrations of benzoic acids and the lowest levels of phenols and aliphatic carboxylic acids. Analytical pyrolysis-GC/MS, a GC/MS technique used to analyze the high-molecular-weight fraction of the extracts (which the regular GC/MS method was incapable of), also validated the predominant presence of benzoic acids in the Battrum ethyl acetate extract through the detection of high levels of benzene in the pyrolytic products.

The GC/MS results of the Fosterton ethyl acetate extract and acidic chromatographic fraction corroborate the NMR finding of the strong presence of benzoic acids, but they also indicate, again in comparison to the other samples, a high level of aliphatic carboxylic acids and a significant amount of phenols. The latter appears to contradict the NMR and the analytical pyrolysis-GC/MS results, both of which would indicate even less phenols present than in the Battrum extract. The infrared analyses of the Fosterton dried permeates and ethyl acetate extracts show the presence of both carboxylic acids and phenols, but the presence of the O-H stretch band at lower frequencies (3100-3000 cm^{-1}) in the Battrum and Fosterton cases could, once again, point to a much higher concentration of carboxylic acids in comparison to phenols.

In other analyses, the Battrum acid number was the highest of the four ethyl acetate extracts followed by that of Fosterton. Both were solely defined by strong acid components, characteristic of carboxylic acids. Excluding the molecular weight of the Battrum ethyl acetate extract (242) from comparison because the extract probably contained inorganic salts, the molecular weight of the Fosterton extract (199) was the highest of the remaining three samples. Finally, of the four extracts investigated by thermal gravimetric analysis, the Battrum and Fosterton extracts exhibited an intermediate volatility.

c) Lone Rock and Meota

At the other end of the sample spectrum are the Lone Rock and Meota steamflood samples. Unfortunately, because of the low yield of the Meota ethyl acetate extract, only infrared and GC/MS analyses could be performed on this product.

The C/H ratio of the Lone Rock ethyl acetate extract is a low 0.74, indicating a more aliphatic character than the previous two fireflood samples. This observation is supported by the ^{13}C NMR analysis, which found no evidence of benzoic acids. According to the NMR data, the Lone Rock extract appeared to primarily consist of acetic acid (69 mol %) and a relatively small phenols component (14 mol %). These results are not supported, however, by the GC/MS data from the Lone Rock ethyl acetate extract and acidic chromatographic fraction. Both sets of data indicate high levels of various phenolic compounds, but only moderate amounts of aliphatic carboxylic acids. In accord with the NMR findings, only trace amounts of benzoic acid were identified by GC/MS.

Analytical pyrolysis-GC/MS of the Lone Rock extracts showed that carbon monoxide was the most abundant pyrolysis product, which would indicate a preponderance of phenols in the extract, in agreement with the other GC/MS results. Infrared analysis of the Lone Rock extract identified both carboxylic acids and phenols, but the shift of the O-H stretch to higher frequencies (3200 cm^{-1}) would, once again, indicate a higher concentration of phenols. The value of the strong acid component in the Lone Rock extract was the lowest among the four extracts and, for the first time, a considerable weak acid component appeared. The mole ratio of carboxylic acids to phenols based on the values of the strong and weak acid components was much lower (3.6) than that implied by the NMR data (5.4). The molecular weight of the Lone Rock extract was slightly lower than that of the Fosterton extract; nevertheless, the Lone Rock sample exhibited by far the lowest volatility of the four extracts.

All of these analyses clearly point to an underestimation by ^{13}C NMR of the phenols content or rather an overestimation of the acetic acid content. The high acetic acid content is not indicated by any of the other analyses. In fact, given the workup procedures using vacuum and/or heat to remove the ethyl acetate solvent, light ends are the first compounds to be lost. This leads to the speculation that the acetic acid may have been formed by hydrolysis of the ethyl acetate solvent, which was identified by NMR to be present in the Lone Rock extract.

Although the various GC/MS data on the Meota sample at first glance may appear to contradict one another in a quantitative sense, the disagreement is most likely non-existent once the MS data are quantified using proper response factors. GC/MS analyses of both the ethyl acetate extract and the acid chromatographic fraction show that benzoic acids were the most abundant component, although the phenols content was considerable as well. On the other hand, the analytical pyrolysis results are similar to those from Lone Rock in that the most abundant product was CO, probably resulting from the decomposition of phenols. However, the Meota extract, when pyrolyzed, produced 50% more benzene than the Lone Rock sample did, proof that substantially more aromatic compounds were present. Considering the high level of CO_2 among the pyrolysis products, there is no doubt that these aromatic products were benzoic acids. Infrared analysis of the Meota ethyl acetate extract also confirmed that more phenols than carboxylic acids were present.

d) Eyehill

The organic matter extracted from the Eyehill fireflood emulsion resembled the Battrum and Fosterton samples in some aspects, but the Lone Rock steamflood sample in most others. The Eyehill ethyl acetate extract had the lowest C/H ratio (0.70), the lowest molecular weight (125), and only a slightly higher strong acid component than the Lone Rock sample. It did not have a weak acid component, however. The extract was the most volatile of the four extracts tested. ^{13}C NMR analysis of the extract revealed the presence of aliphatic carboxylic acids (58 mol %), phenols (21 mol %) and benzoic acids (20 mol %). The Eyehill extract thus contained substantially less benzoic acids and considerably more phenols and aliphatic carboxylic acids than the Battrum and Fosterton fireflood samples. The GC/MS analyses of the ethyl acetate extract and acidic chromatographic fraction appear to confirm these findings. The highest abundance was measured for the phenols, followed by the aliphatic carboxylic acids and a moderate amount of benzoic acids. The infrared data on the Eyehill extract also indicated a higher phenol to carboxylic acid ratio compared to the Battrum and Fosterton extracts. As was the case with the Meota sample, the analytical pyrolysis-GC/MS results appear to contradict the direct GC/MS data in that benzene was the most abundant pyrolytic product (indicating a possible preponderance of benzoic acids). Of the three fireflood extracts the Eyehill sample produced the most CO, showing it to be richer in phenols in confirmation of the direct GC/MS data. Again, in these cases where important species appear to occur in comparable quantities, more rigorous quantification of the GC/MS data is needed before conclusions can be drawn.

Summarizing the above results, it can be concluded that the organic materials extracted from the Battrum and Fosterton emulsions consisted mainly of benzoic acids, aliphatic carboxylic acids and some phenols. The Lone Rock extract contained mainly phenols and aliphatic carboxylic acids, while the Eyehill and Meota samples were situated in between.

SURFACE ACTIVITY OF ISOLATED COMPOUNDS

The objectives of this study went further, however, than solely characterizing the dissolved organic matter extracted from the wellhead emulsions. The objectives were to isolate and characterize the emulsion-stabilizing surfactants occurring in these fluids. What remains to be shown, therefore, is that the isolated organic material does indeed have emulsion-stabilizing properties. Unfortunately, this could not be proven explicity. In much of the literature a lowering of the interfacial tension between the two immiscible phases is believed to be conducive to emulsion stability. Hence, measurements of the interfacial tension between a surfactant-free wellhead oil and an aqueous phase, with and without the organic material to be tested on its surfactant properties, would be required. This type of experiment has been difficult to implement, however.

First, the wellhead oil would have to be free of water and, second, it should not already contain the surfactant material to be tested. While washing the oil repeatedly with water may possibly help meet the second condition, dewatering the oil, especially the light fireflood emulsions, is nearly an impossible goal, if demulsifiers cannot be used. Third, the surfactant material to be tested would have to be dissolved in the water phase as a way of introducing it into the oil/water system. It is the latter problem that became immediately obvious, once the ethyl acetate extracts were obtained: they were insoluble in water, possibly because of the loss of light ends during the workup process.

Hence, it was decided to use the raw permeates for the interfacial tension measurements, since the permeates already contained the organic material, albeit in low concentrations. In order to at least partially meet the conditions regarding the reference oil, it was decided to use a mineral oil as an alternative. The results of the measurements, discussed in Section 3.2.6, were ambiguous and inconclusive. The Battrum and Meota permeates were the most effective in lowering the interfacial tension, followed by Lone Rock. The Fosterton permeate had no effect and the Eyehill permeate increased the interfacial tension.

More work is needed to establish the relationships between the chemical nature/composition of surfactant material and its effect on interfacial tension and, ultimately, its effect on emulsion stability.

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APPENDIX A

^{13}C NMR Spectra of Ethyl Acetate Extracts

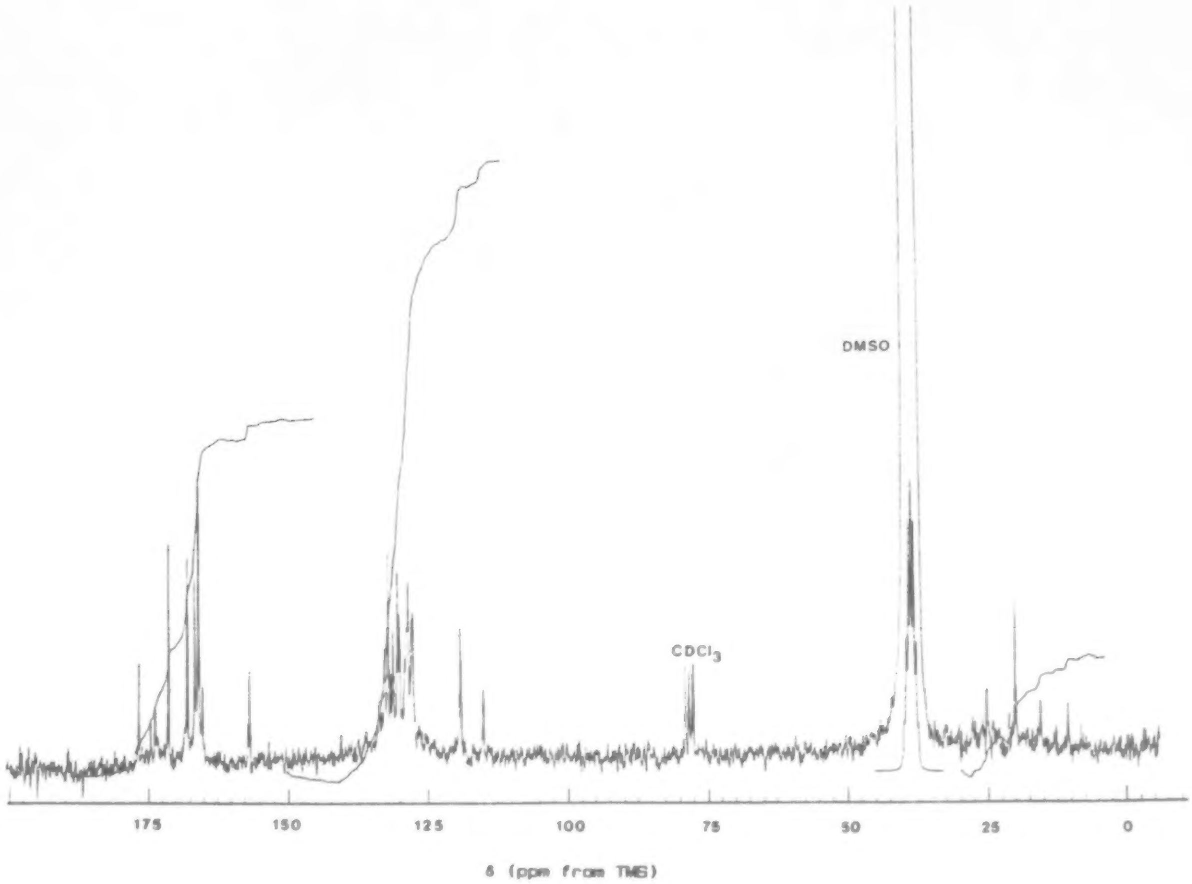

Figure A-1 ^{13}C NMR Spectrum of Battrum Ethyl Acetate Extract

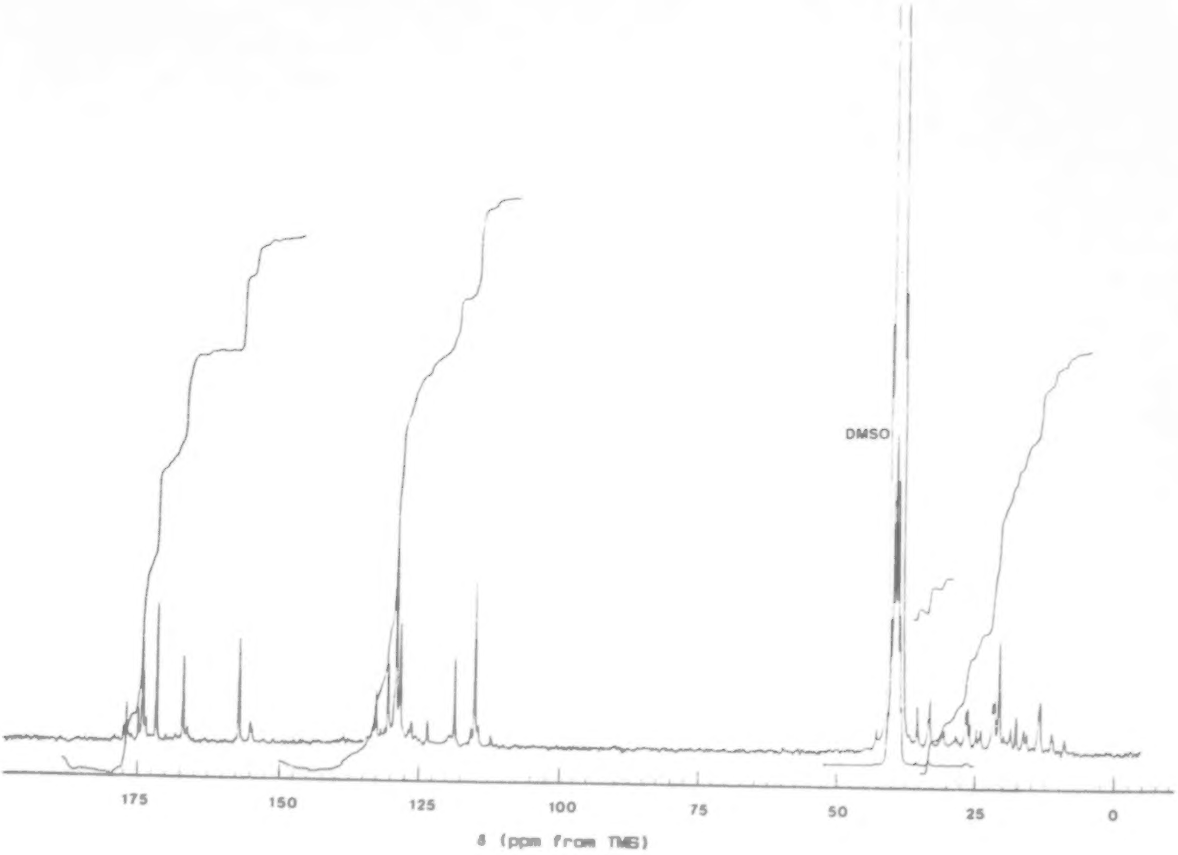

Figure A-2 ¹³C NMR Spectrum of Eyehill Ethyl Acetate Extract

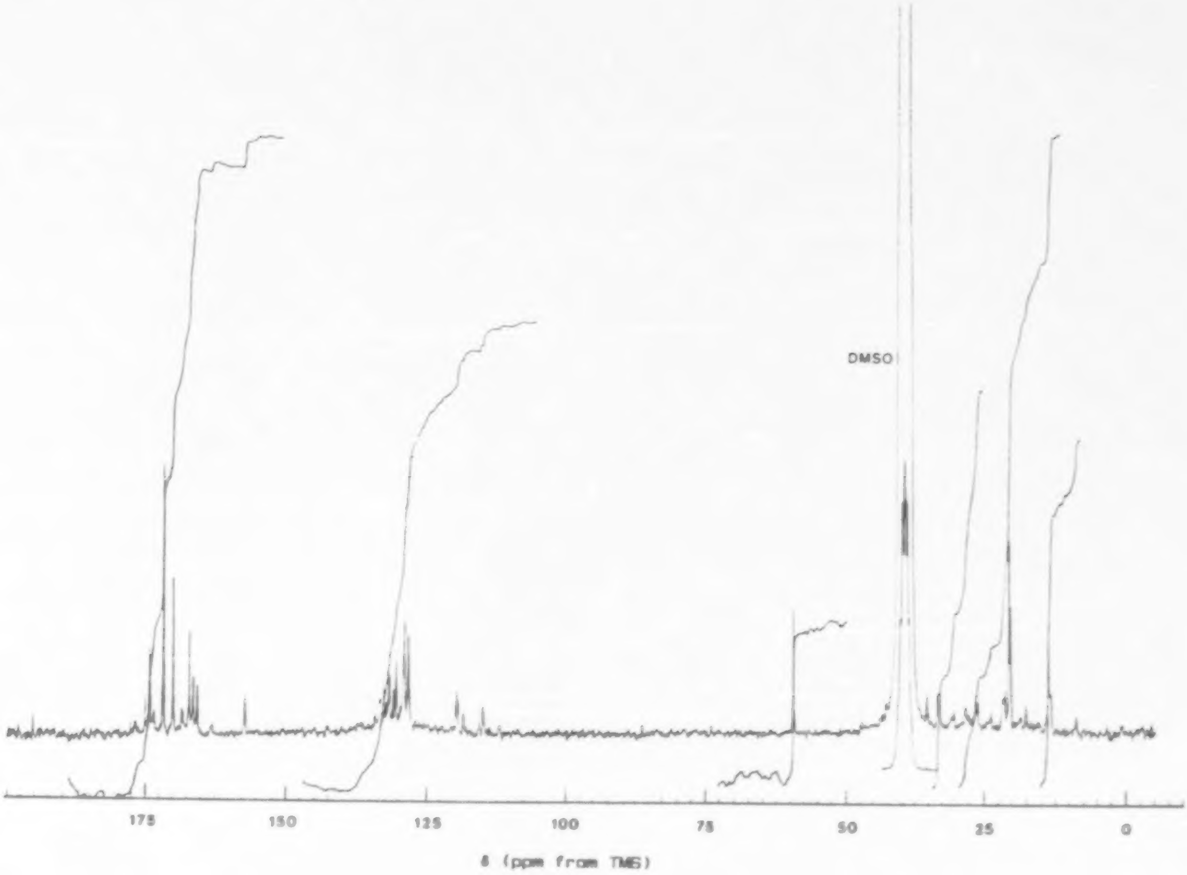

Figure A-3 ^{13}C NMR Spectrum of Fosterton Ethyl Acetate Extract

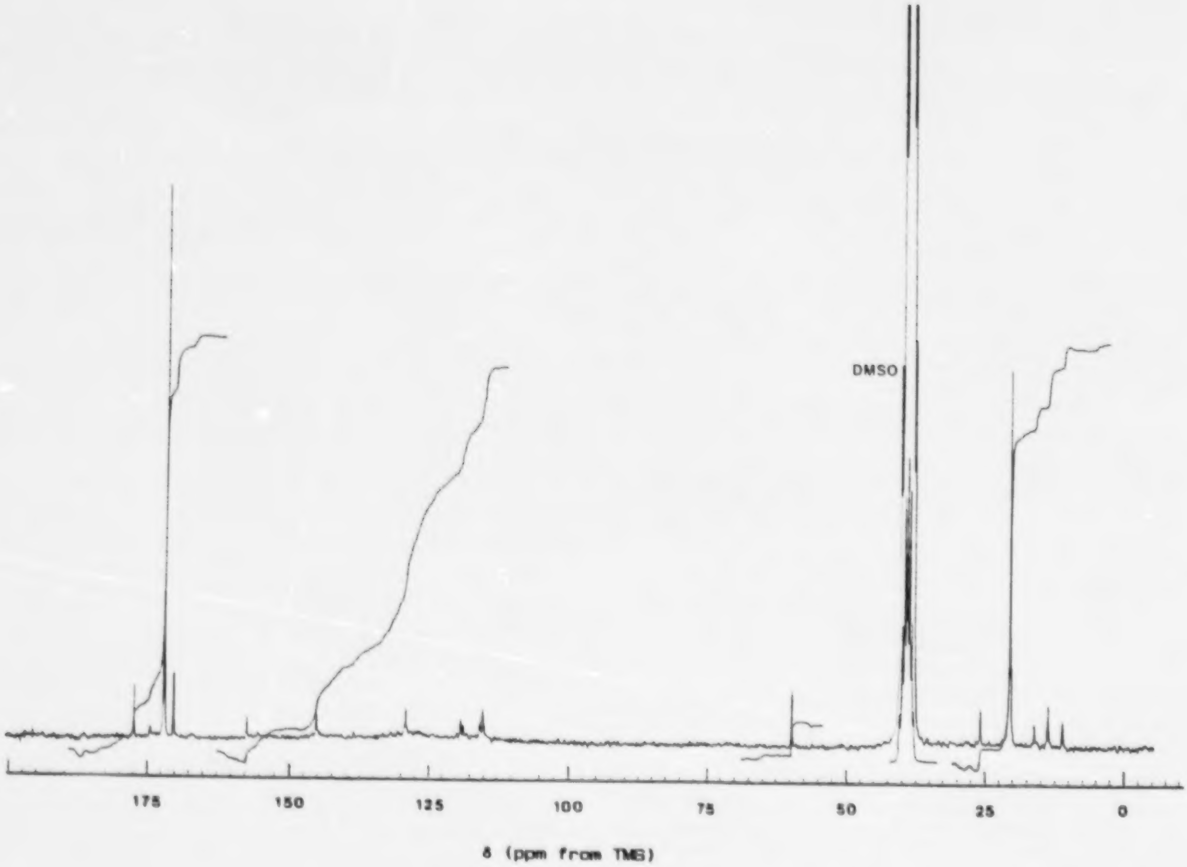

Figure A-4 ^{13}C NMR Spectrum of Lone Rock Ethyl Acetate Extract

APPENDIX B

Infrared Spectra of:

- Dried Permeates
- Acid Precipitates
- Ethyl Acetate Extracts
- Acidic, Neutral and Basic Chromatographic Fractions

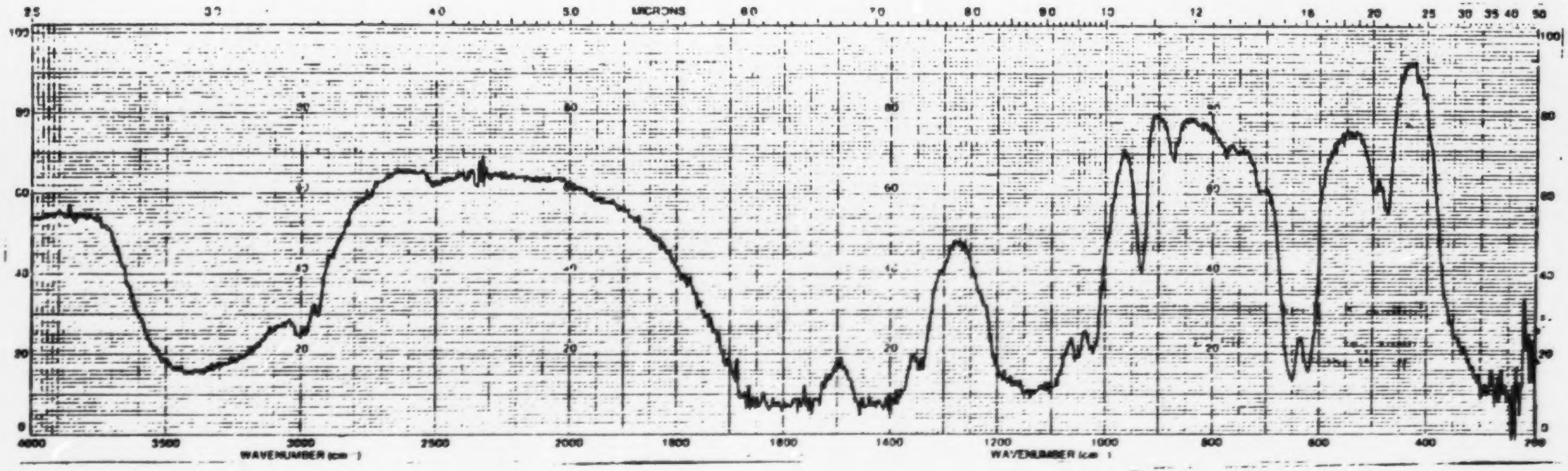

Figure B-1 Infrared Spectrum of Battrum Dried Permeate

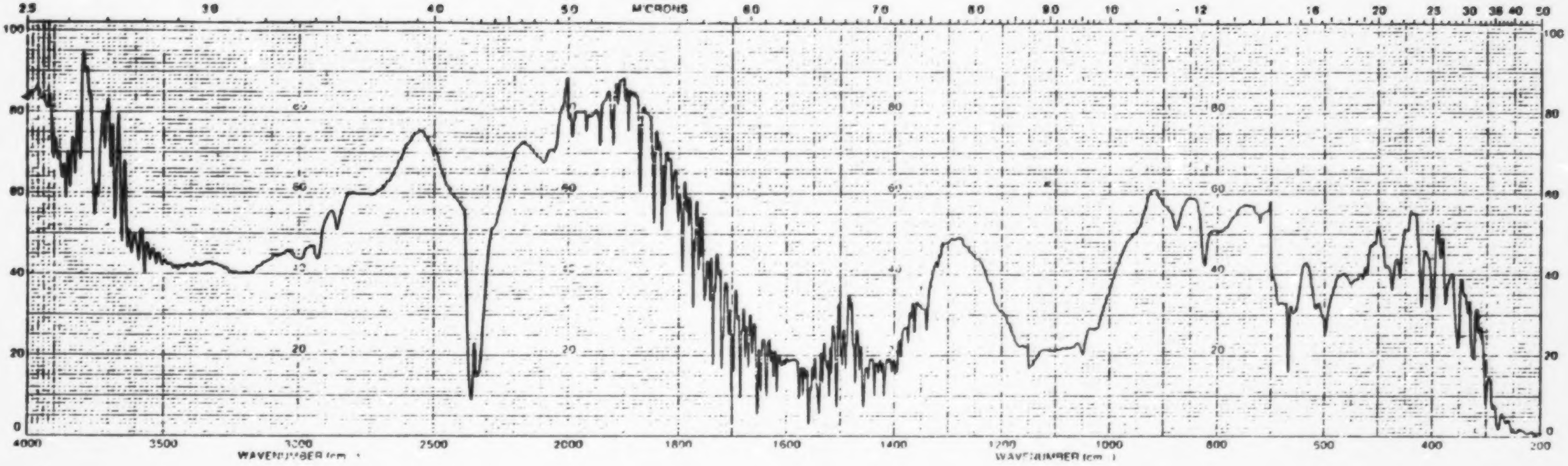

Figure B-2 Infrared Spectrum of Eyehill Dried Permeate

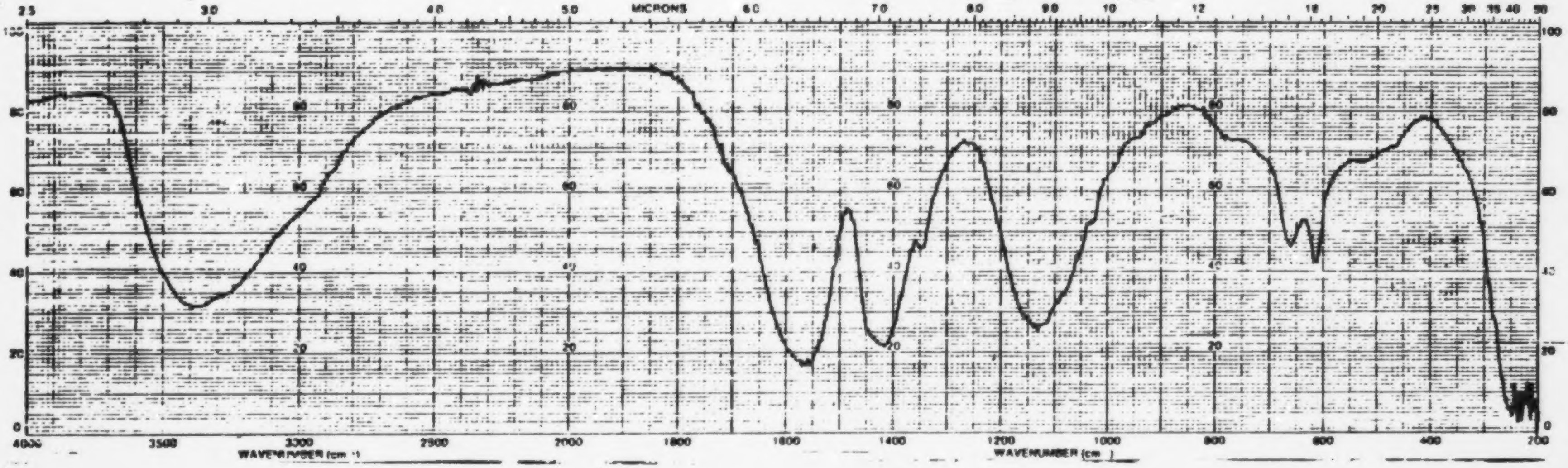

Figure B-3 Infrared Spectrum of Fosterton Dried Permeate

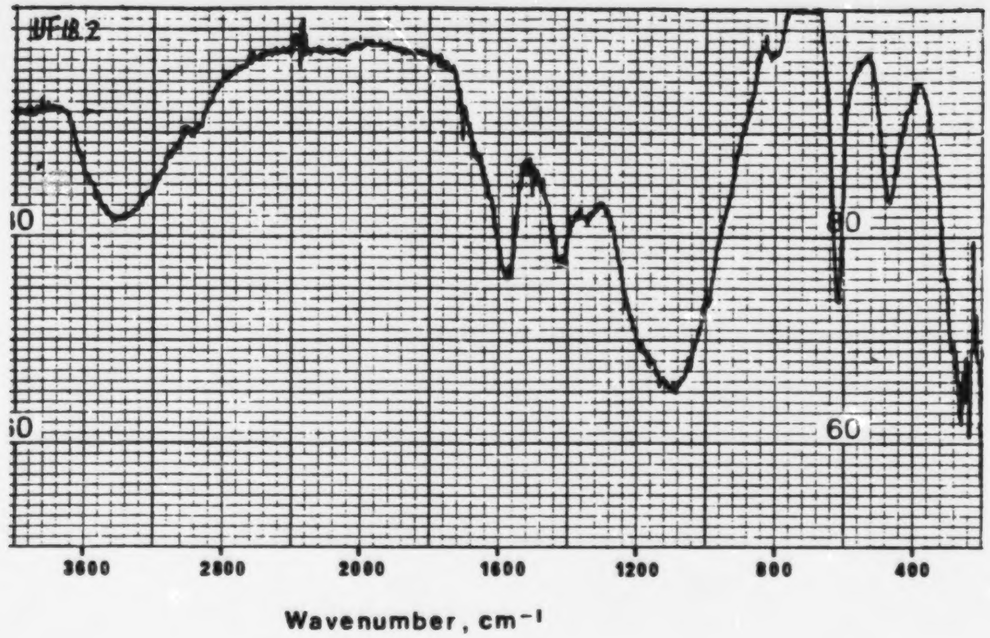

Figure B-4 Infrared Spectrum of Lone Rock (Unaged) Dried Permeate

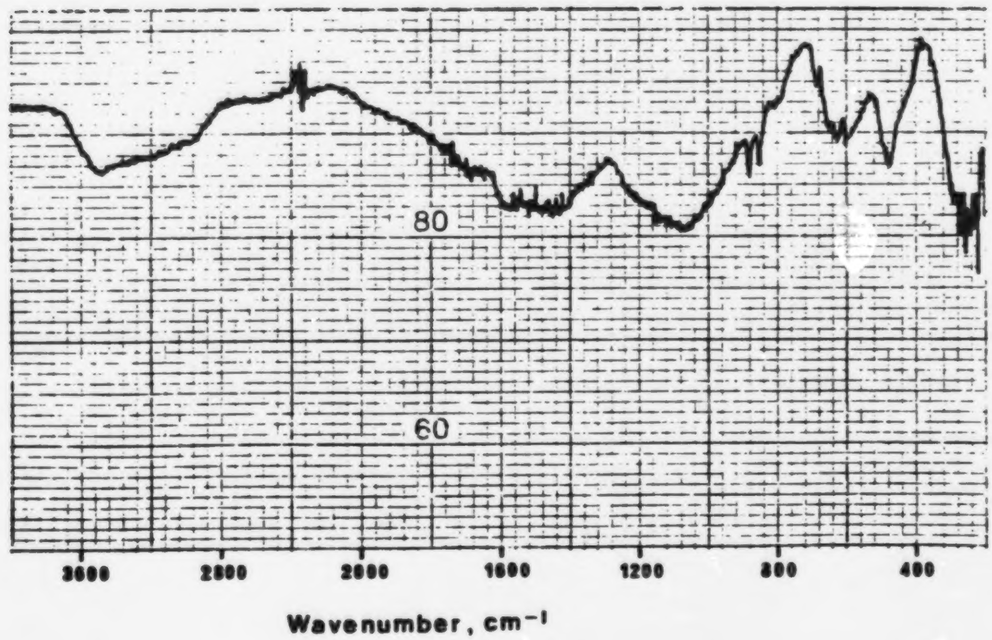

Figure B-5 Infrared Spectrum of Meota Dried Permeate

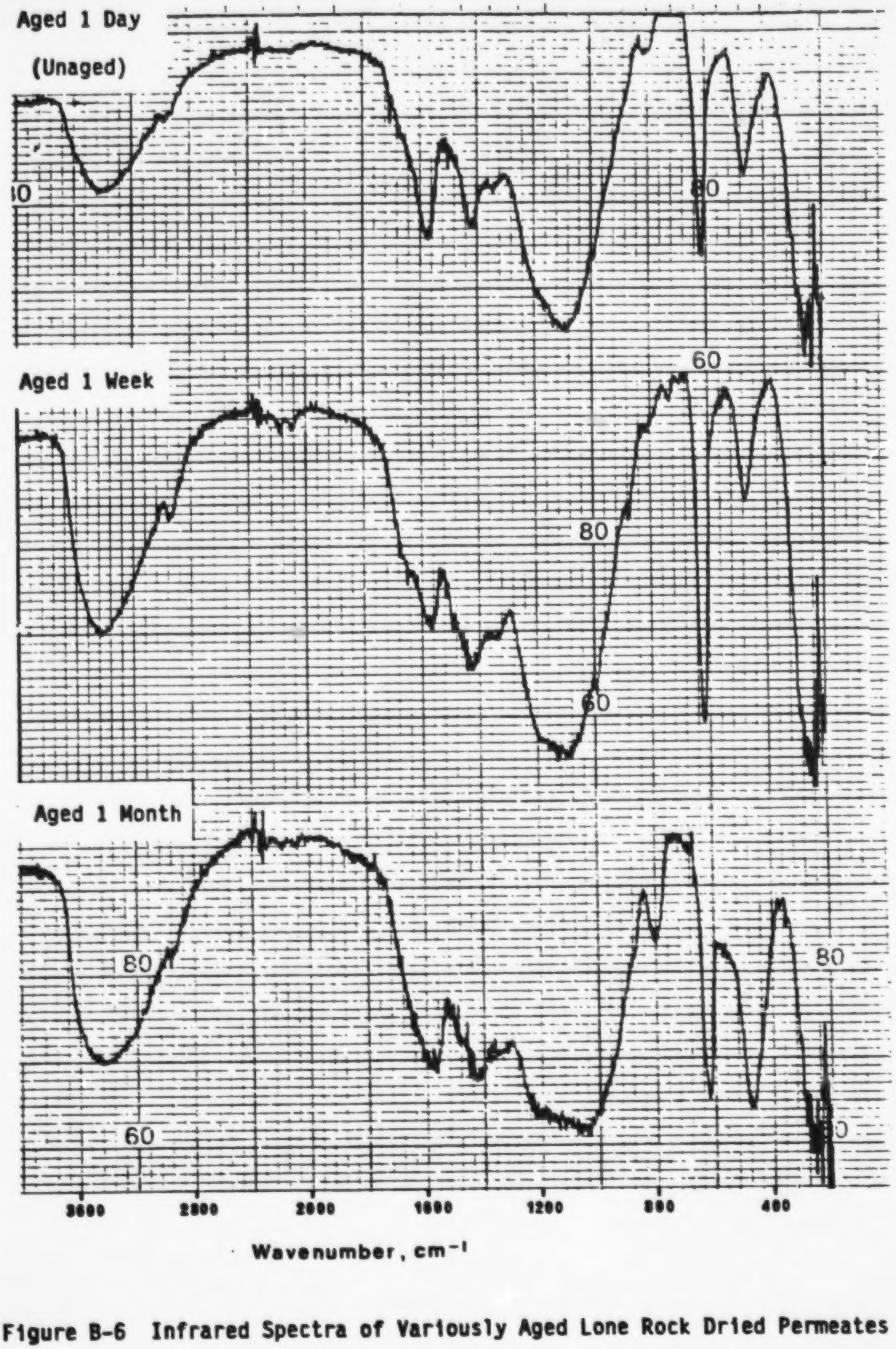

Figure B-6 Infrared Spectra of Variously Aged Lone Rock Dried Permeates

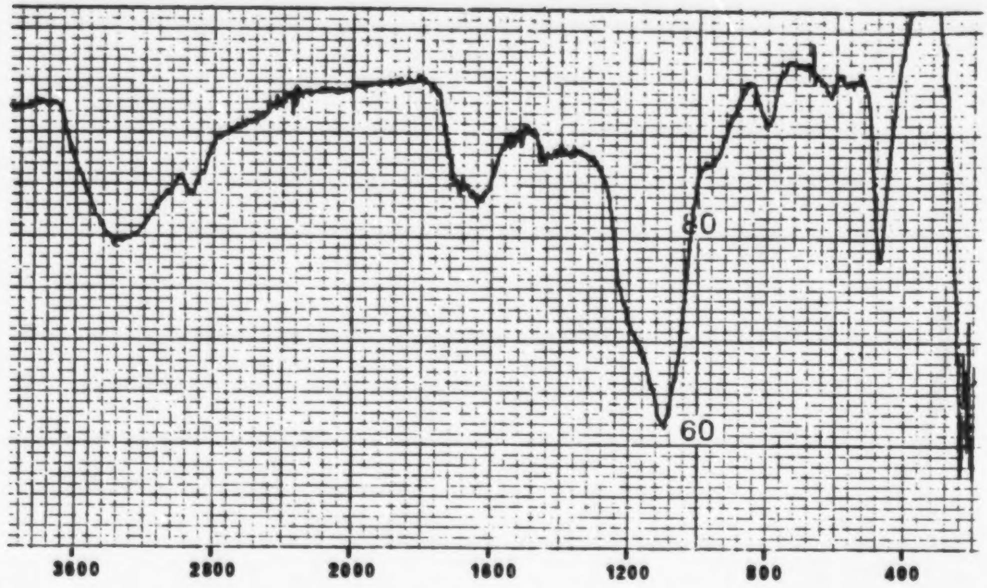

Figure B-7 Infrared Spectrum of Lone Rock (Unaged) Acid Precipitate

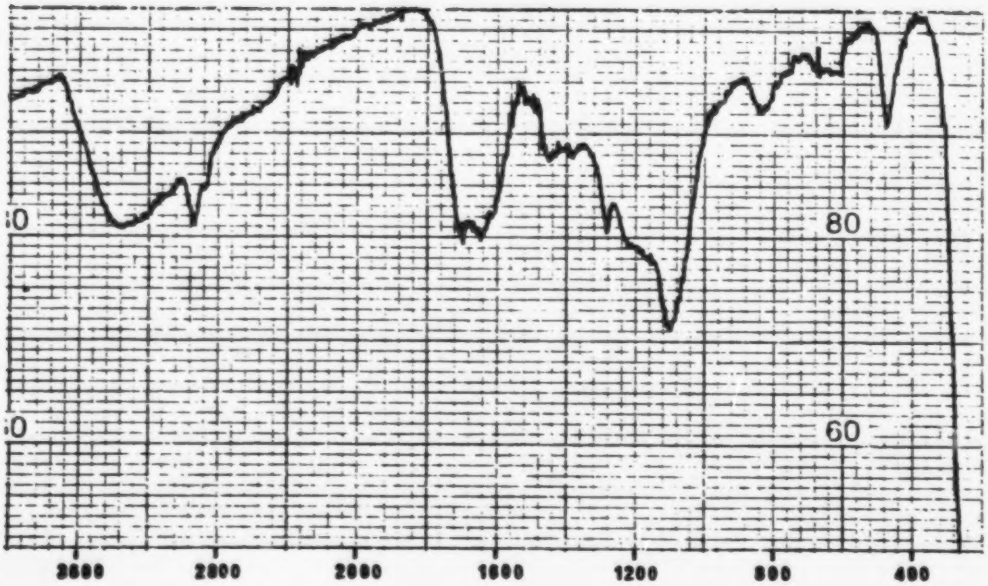

Figure B-8 Infrared Spectrum of Meota Acid Precipitate

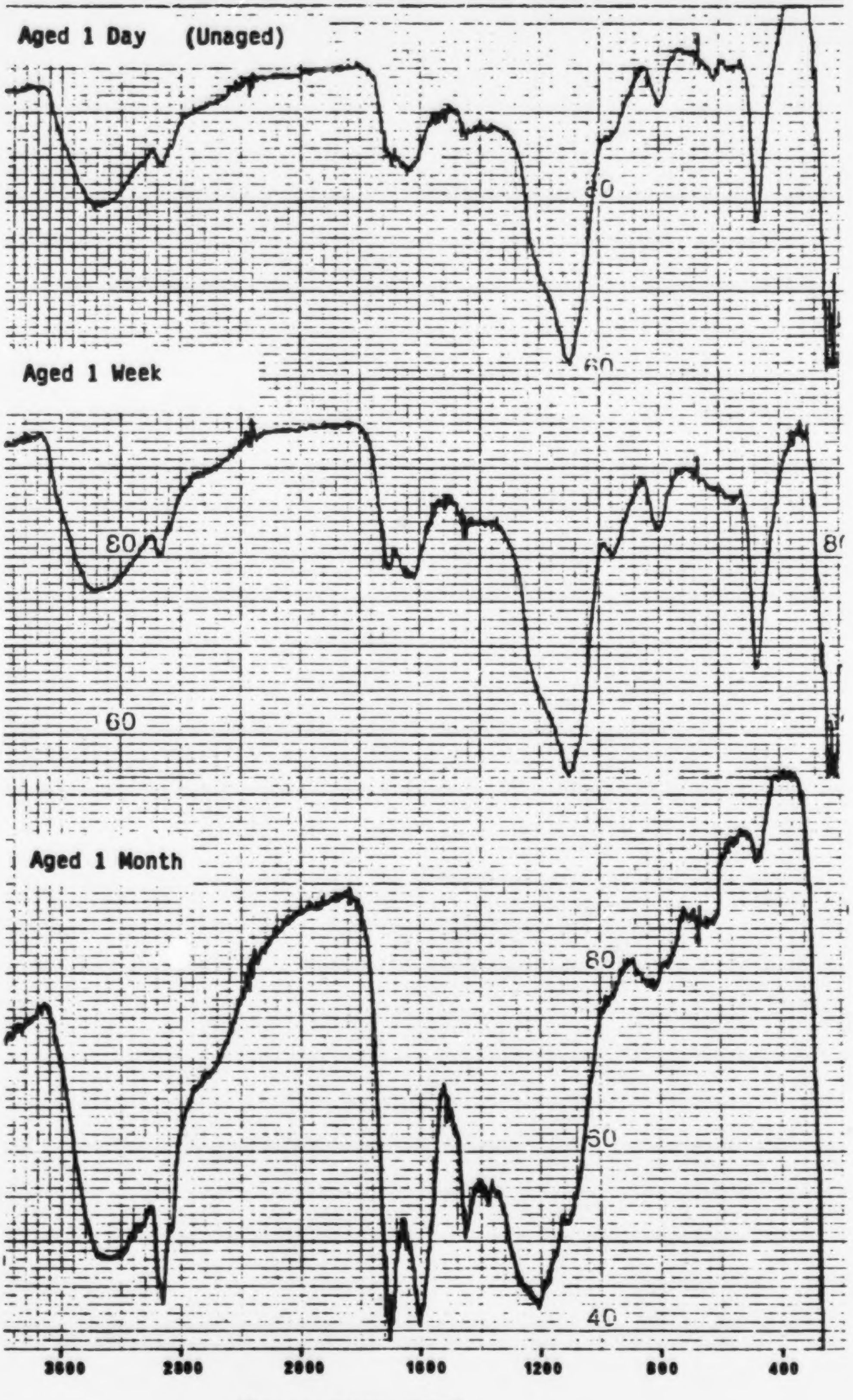

Figure B-9 Infrared Spectra of Variously Aged Lone Rock Acid Precipitates

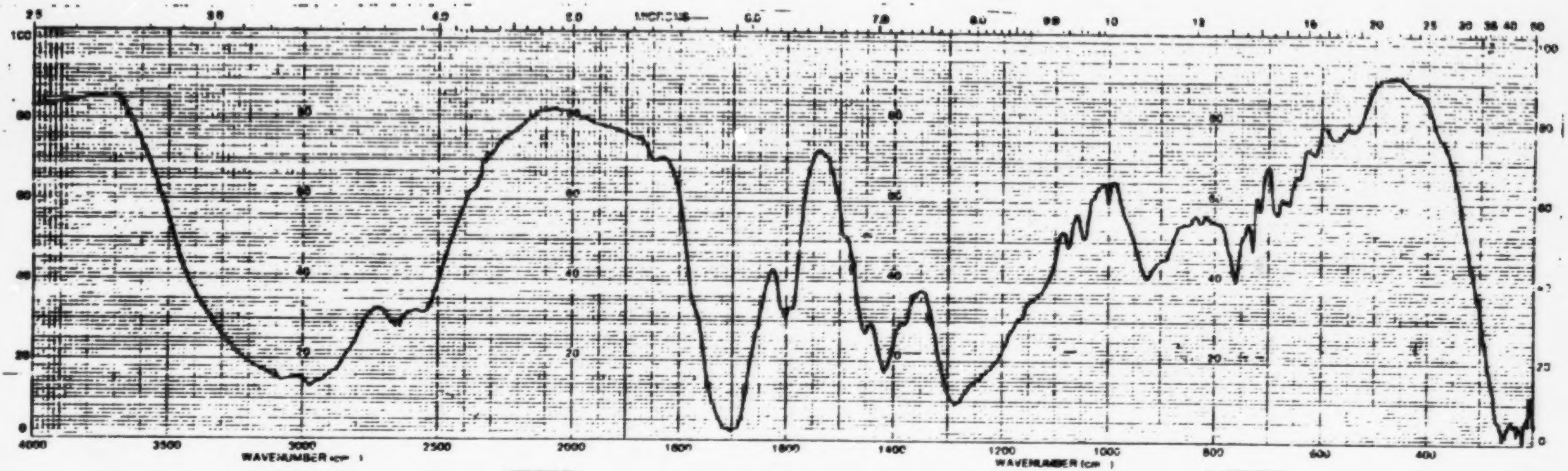

Figure B-10 Infrared Spectrum of Battrum Ethyl Acetate Extract

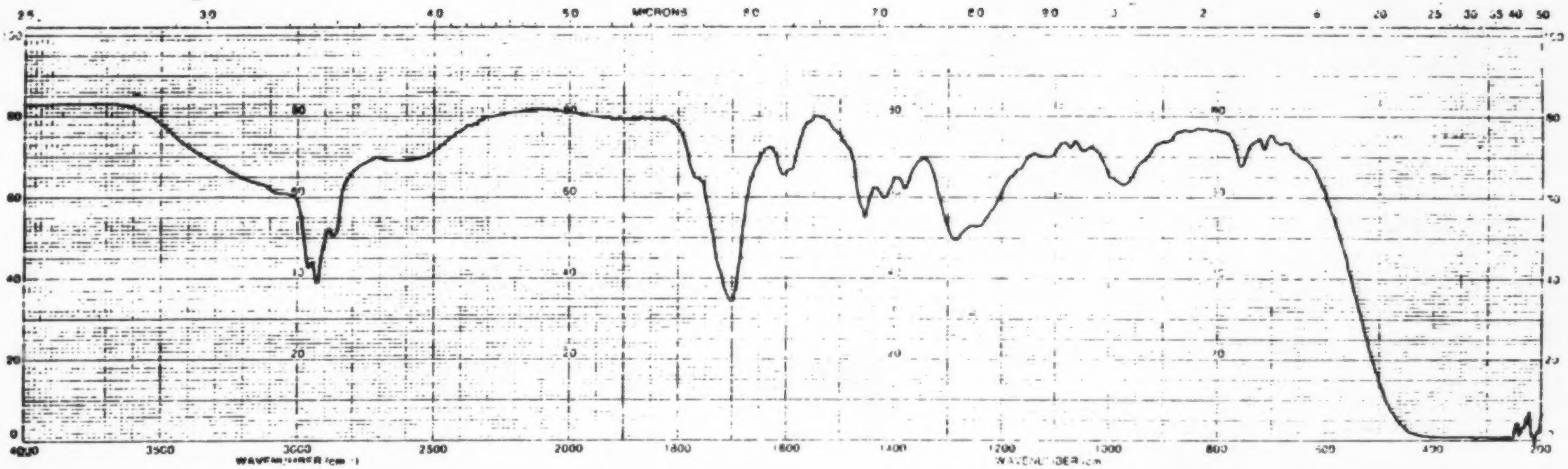

Figure B-11 Infrared Spectrum of Eyehill Ethyl Acetate Extract

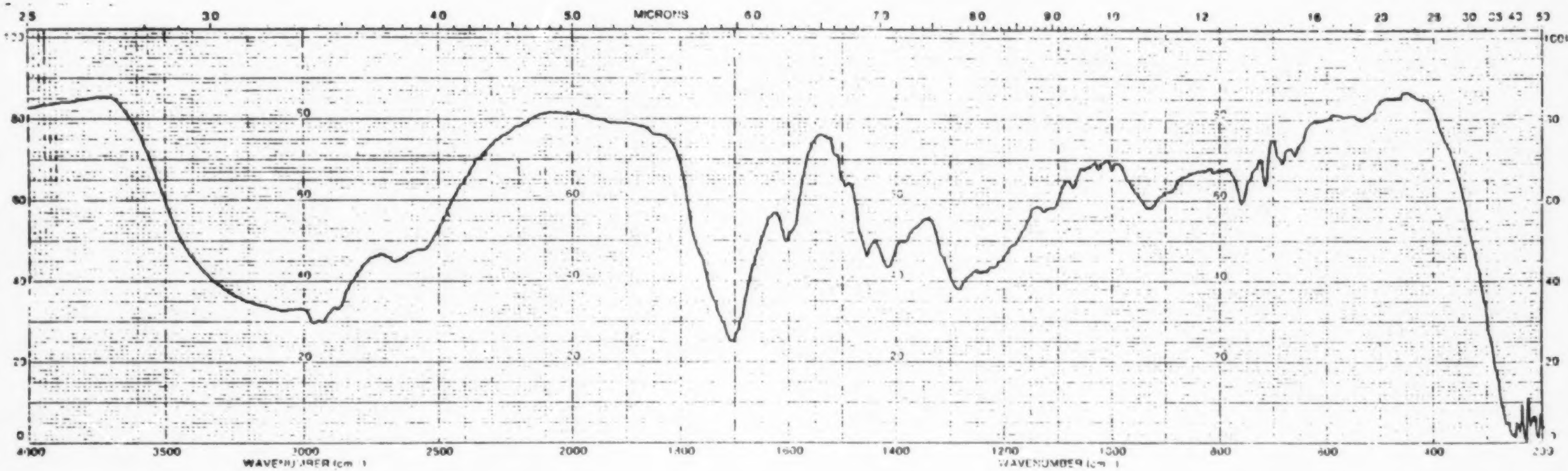

Figure B-12 Infrared Spectrum of Fosterton Ethyl Acetate Extract

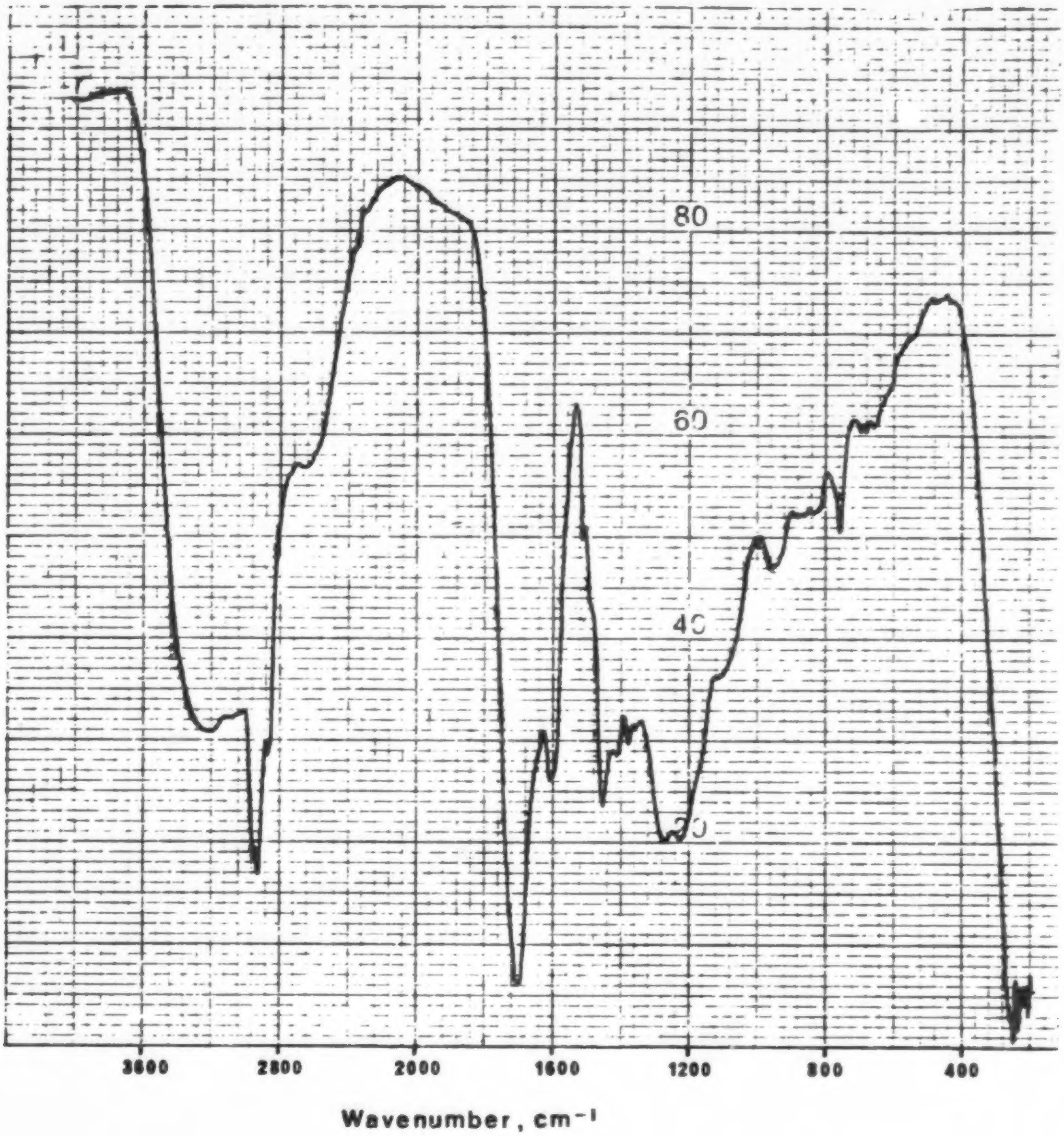

Figure B-13 Infrared Spectrum of Lone Rock (Unaged) Ethyl Acetate Extract

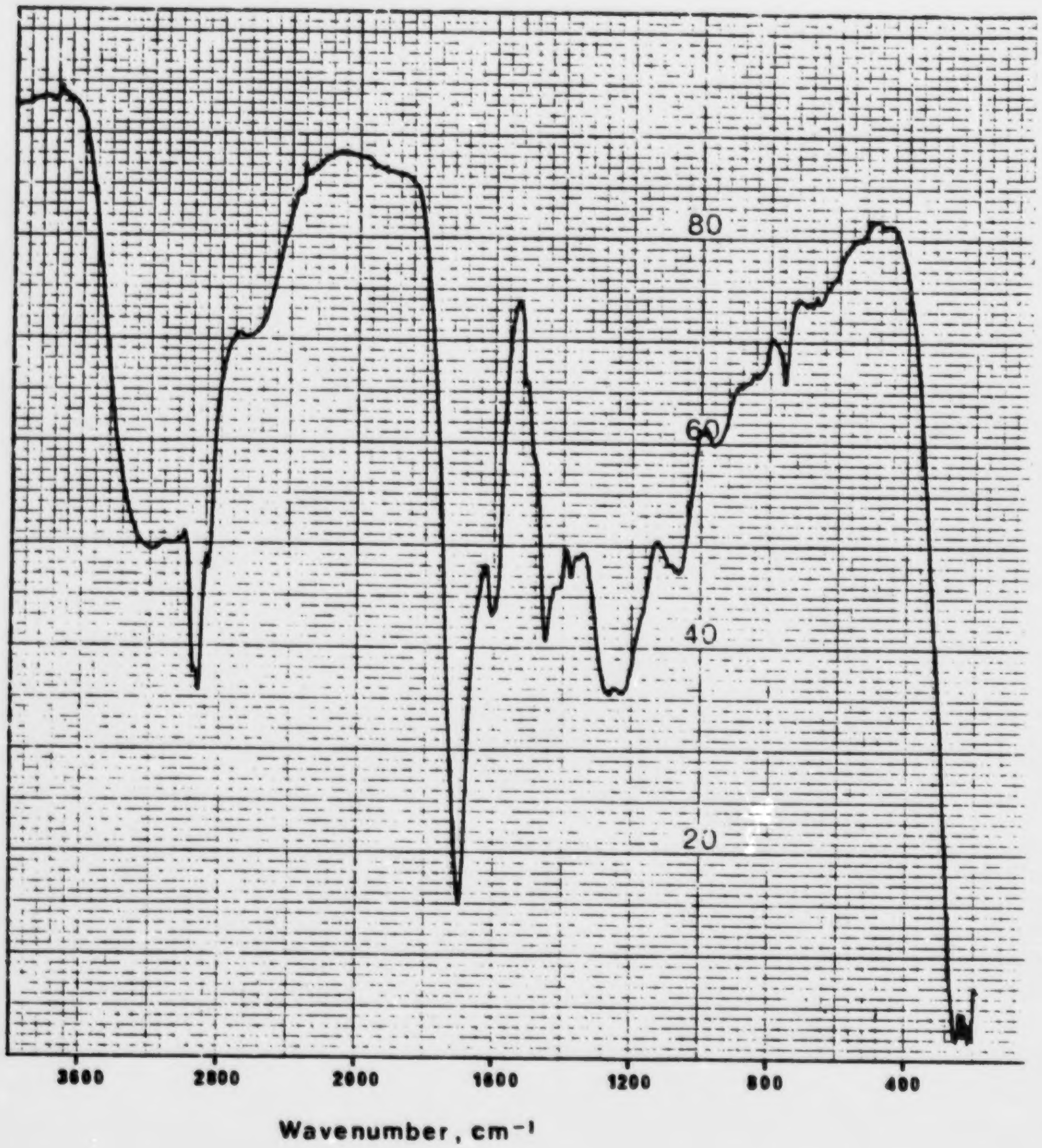

Figure B-14 Infrared Spectrum of Lone Rock (Aged 1 Week) Ethyl Acetate Extract

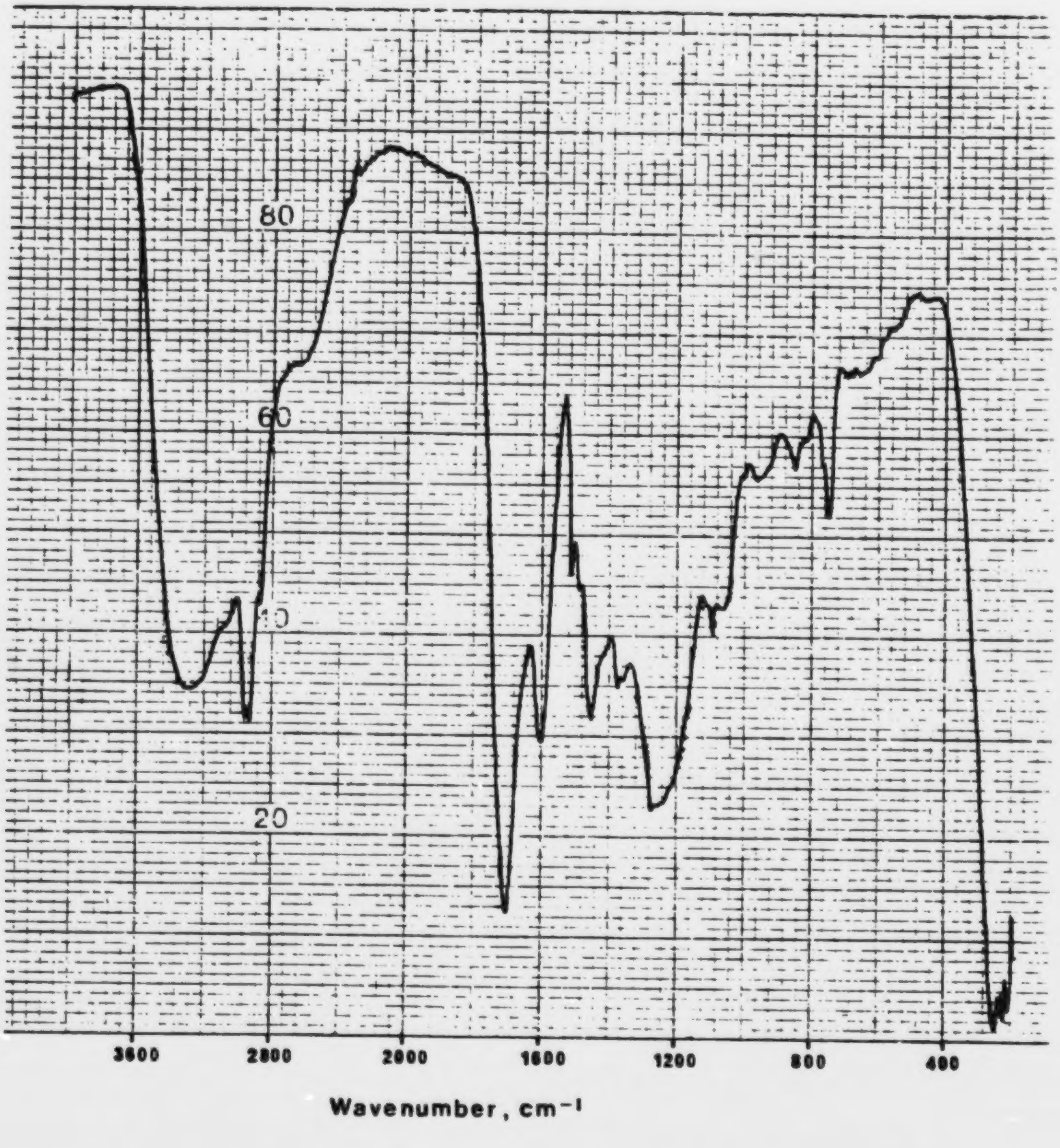

Figure B-15 Infrared Spectrum of Lone Rock (Aged 1 Month) Ethyl Acetate Extract

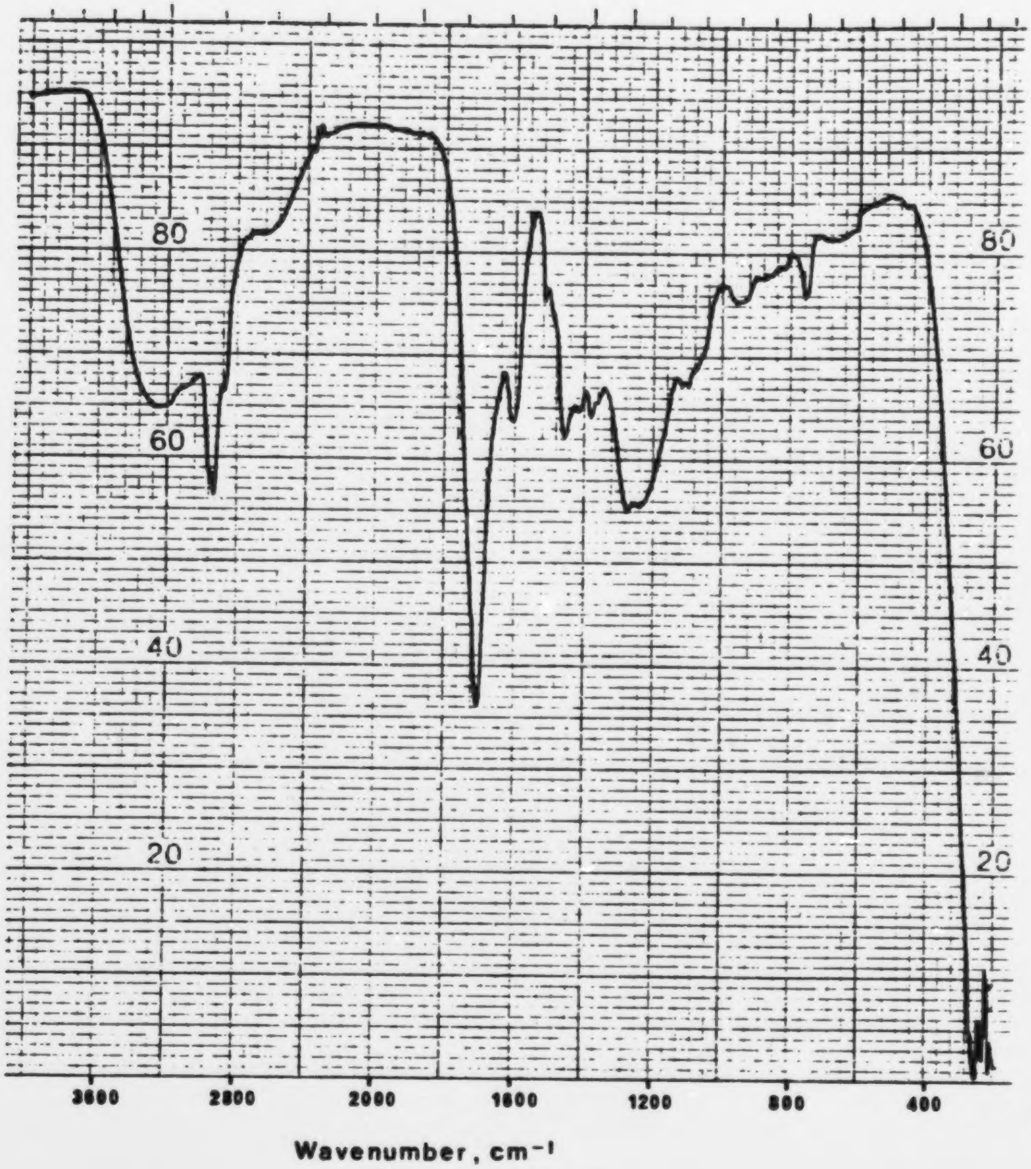

Figure B-16 Infrared Spectrum of Meota Ethyl Acetate Extract

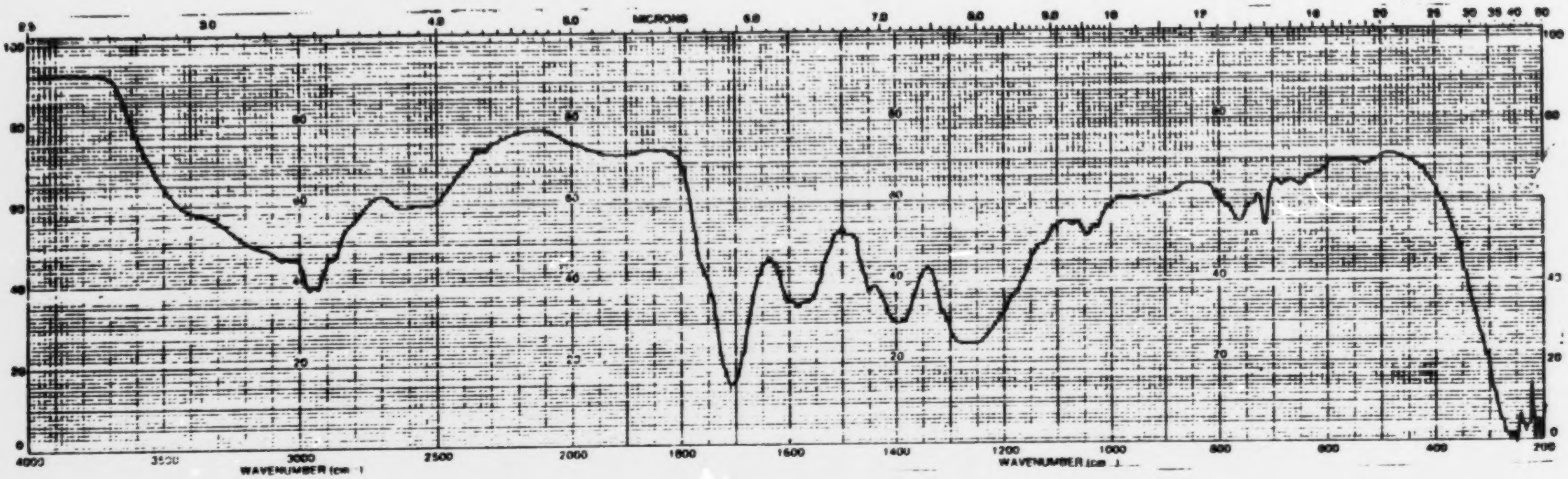

Figure B-17 Infrared Spectrum of the Battrum Acidic Fraction from Chromatography

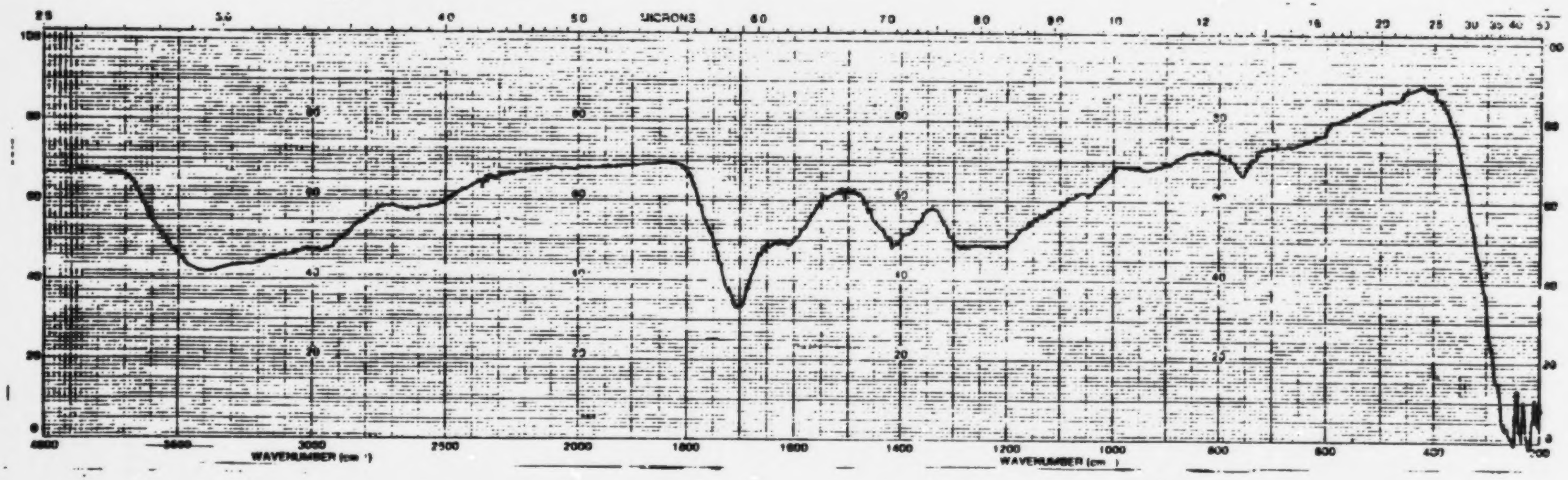

Figure B-18 Infrared Spectrum of the Eyehill Acidic Fraction from Chromatography

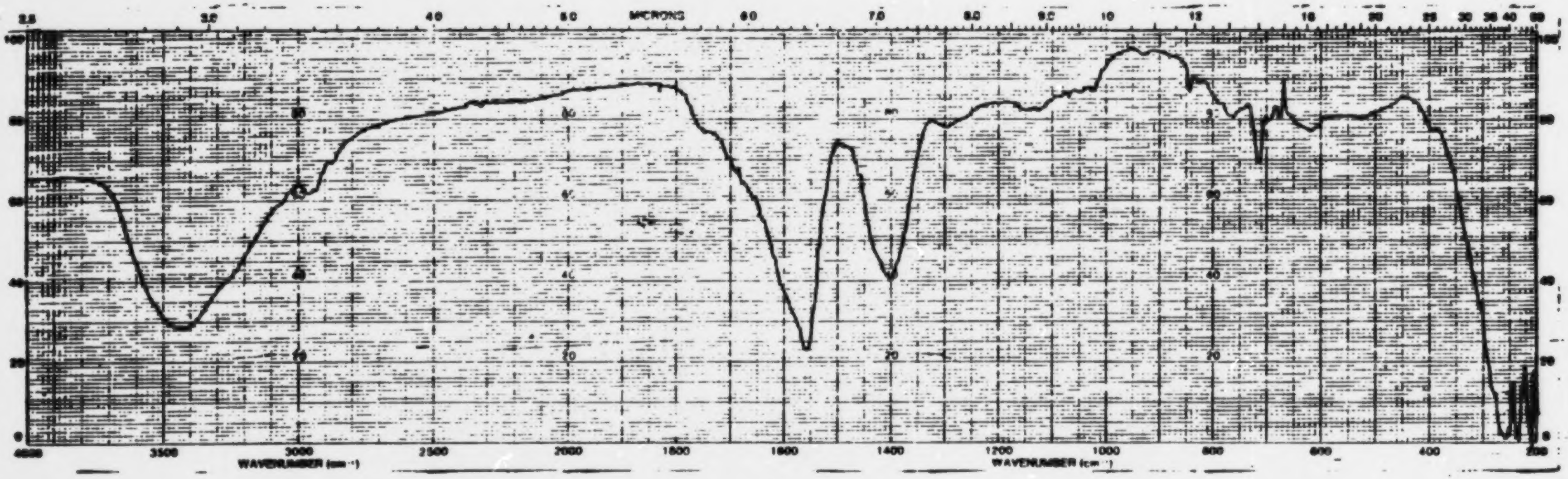

Figure B-19 Infrared Spectrum of the Fosterton Acidic Fraction From Chromatography

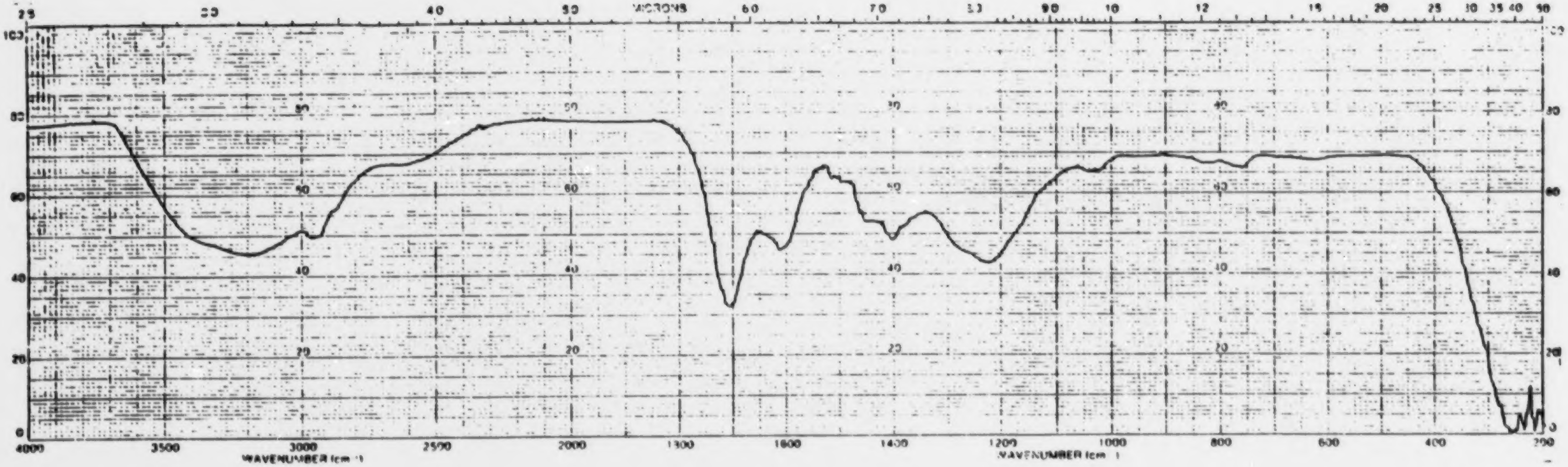

Figure B-20 Infrared Spectrum of the Lone Rock (Unaged) Acidic Fraction From Chromatography

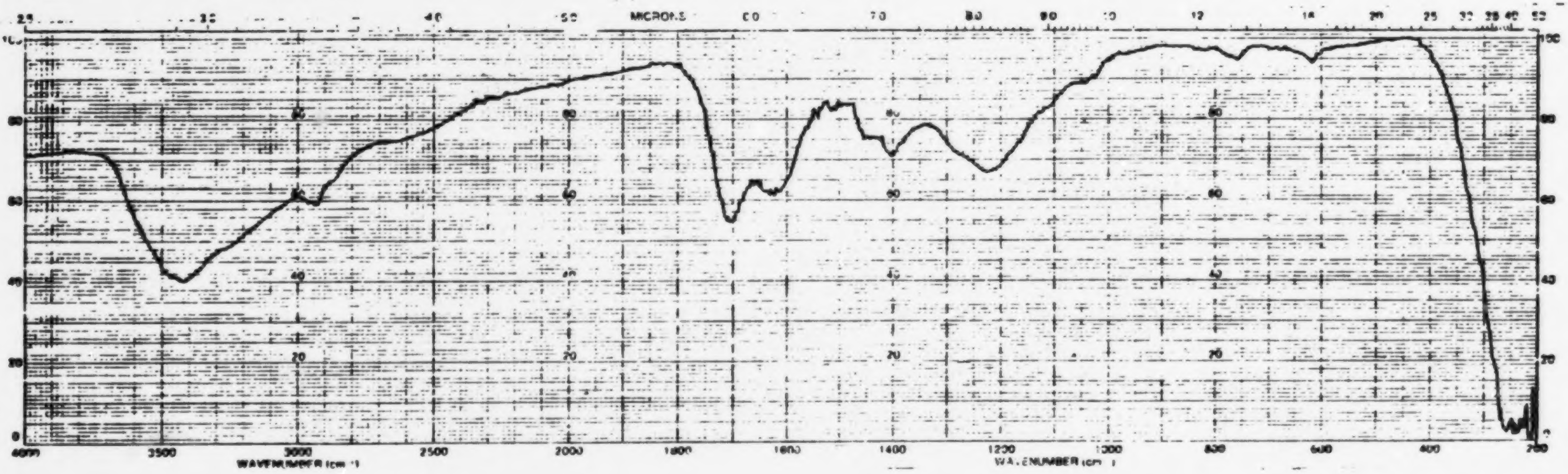

Figure B-21 Infrared Spectrum of the Meota Acidic Fraction From Chromatography

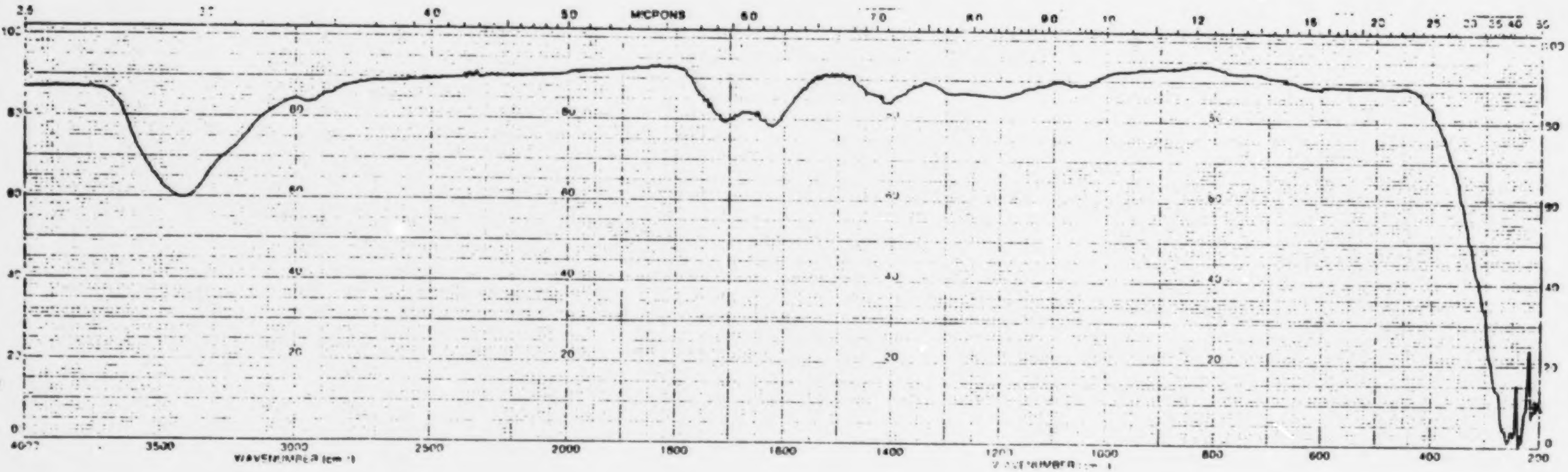

Figure B-22 Infrared Spectrum of the Battrum Neutral Fraction (N_1) From Chromatography.

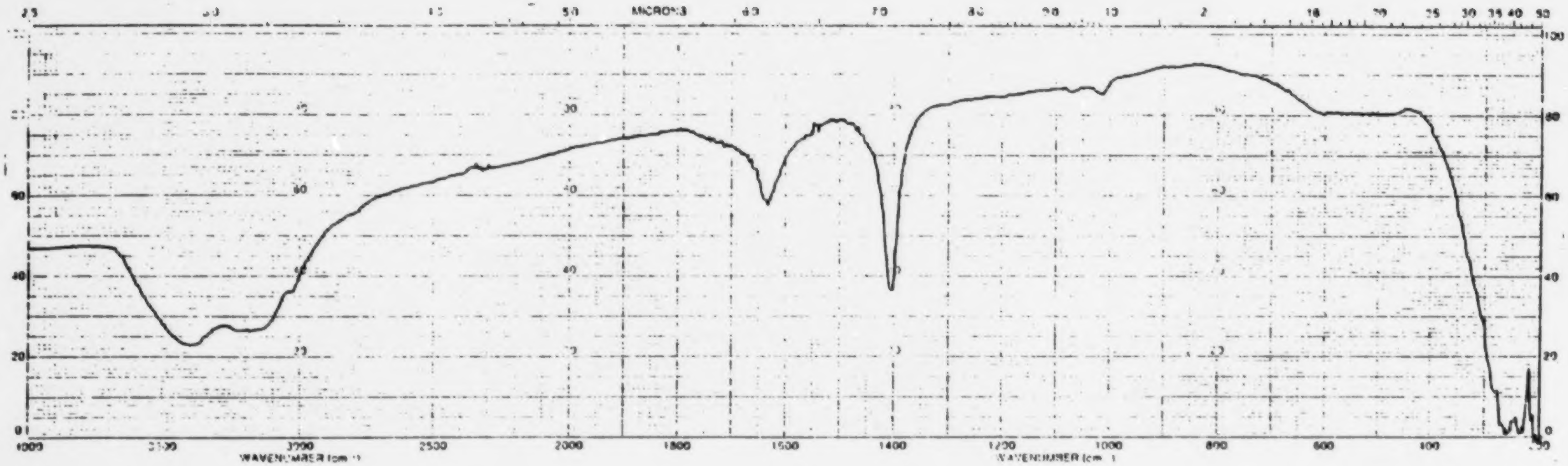

Figure B-23 Infrared Spectrum of the Eyehill Neutral Fraction (N_1) From Chromatography.

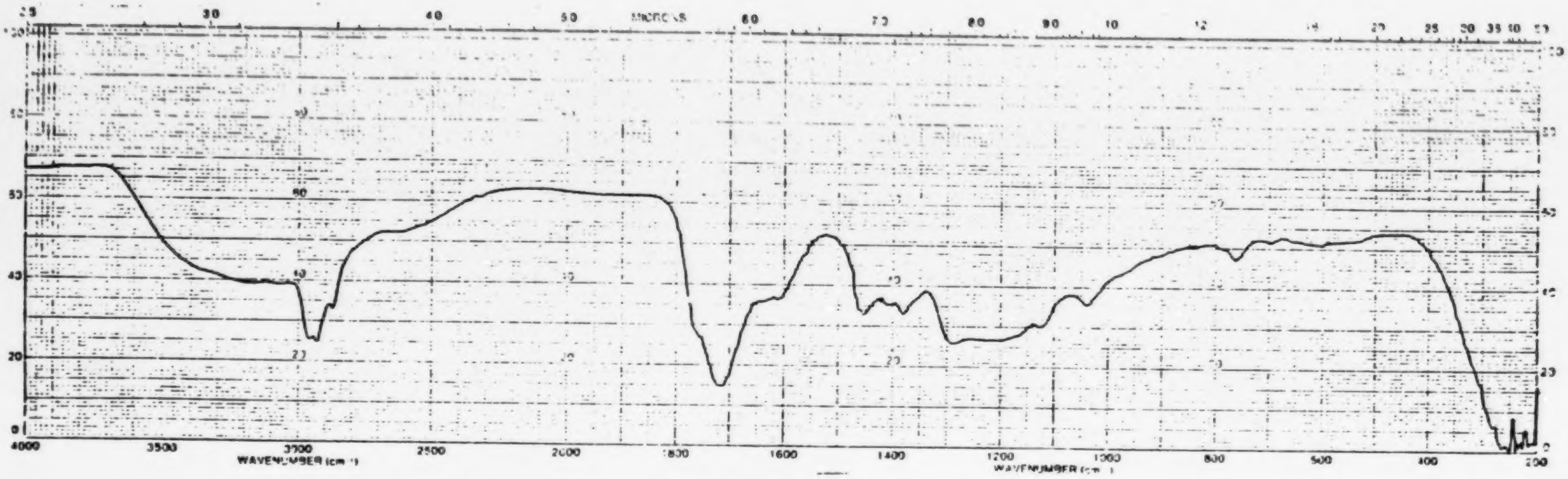

Figure B-24 Infrared Spectrum of the Fosterton Neutral Fraction (N_1) From Chromatography.

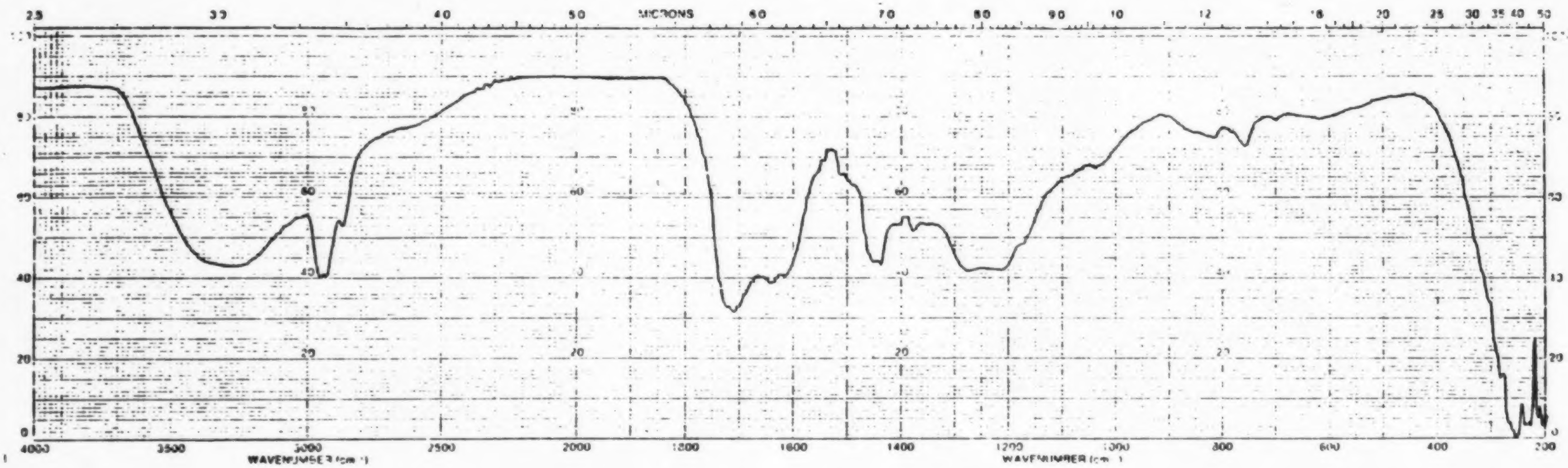

Figure B-25 Infrared Spectrum of the Lone Rock Neutral Fraction (N_1) From Chromatography.

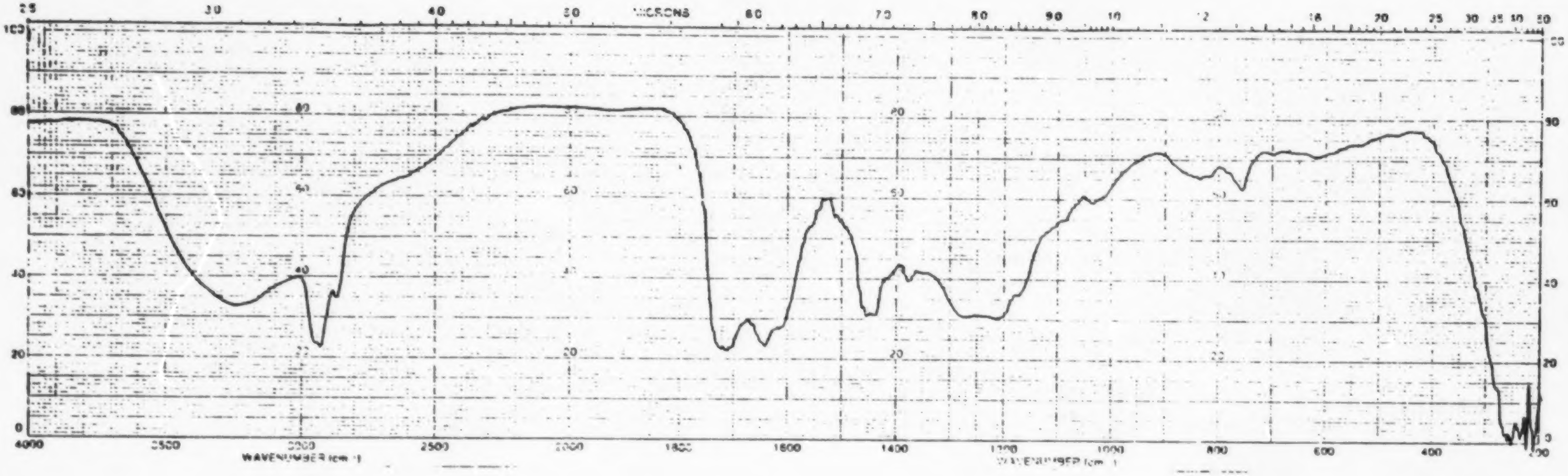

Figure B-26 Infrared Spectrum of the Meota Neutral Fraction (N_1) From Chromatography.

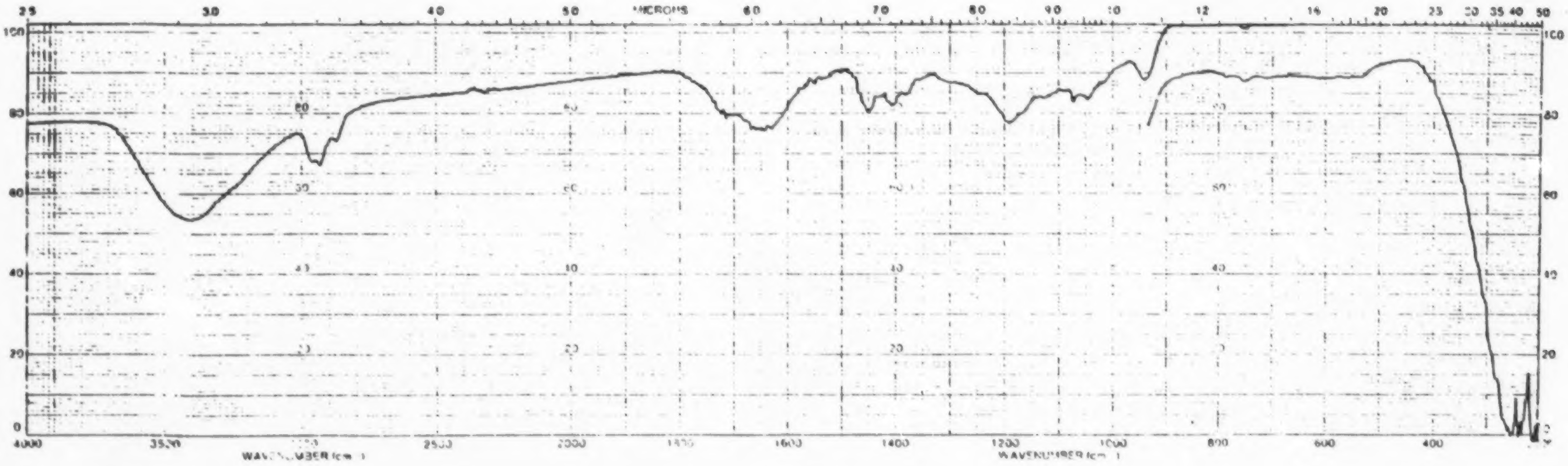

Figure B-27 Infrared Spectrum of the Eyehill Neutral Fraction (N_2) From Chromatography.

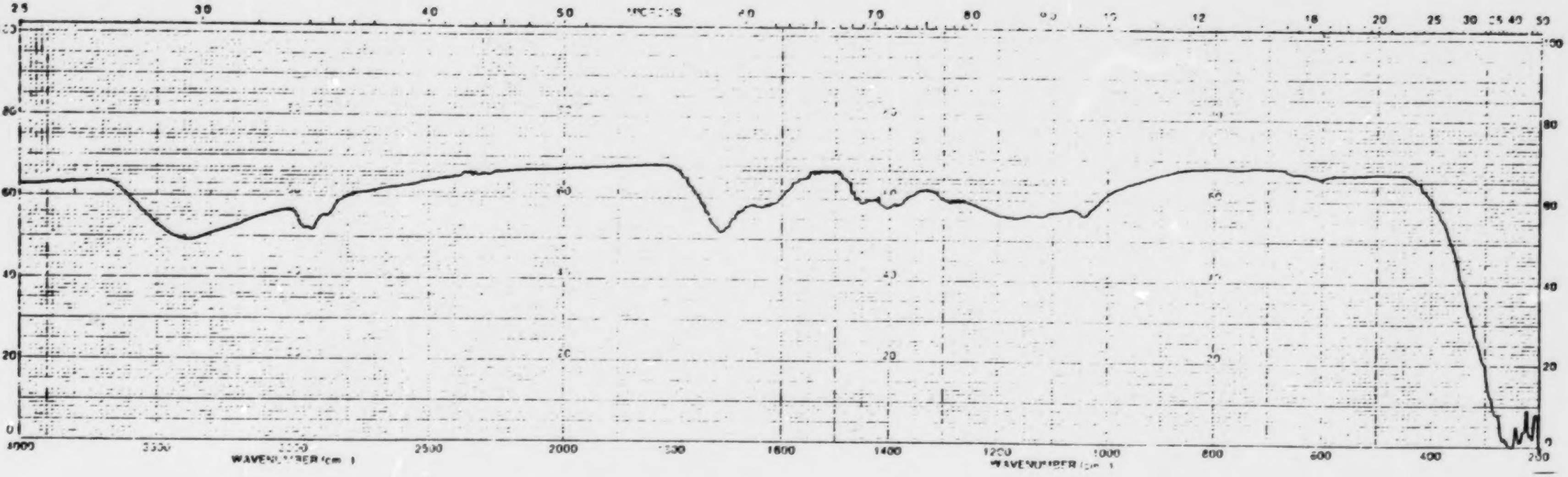

Figure B-28 Infrared Spectrum of the Fosterton Neutral Fraction (N_2) From Chromatography.

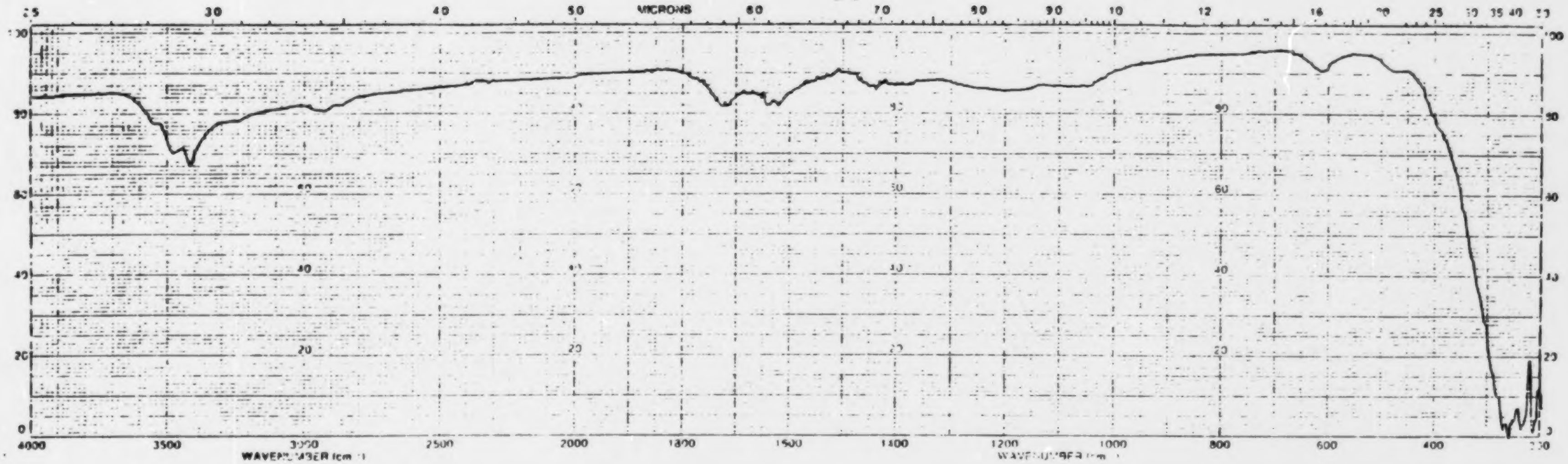

Figure B-29 Infrared Spectrum of the Lone Rock Neutral Fraction (N_2) From Chromatography.

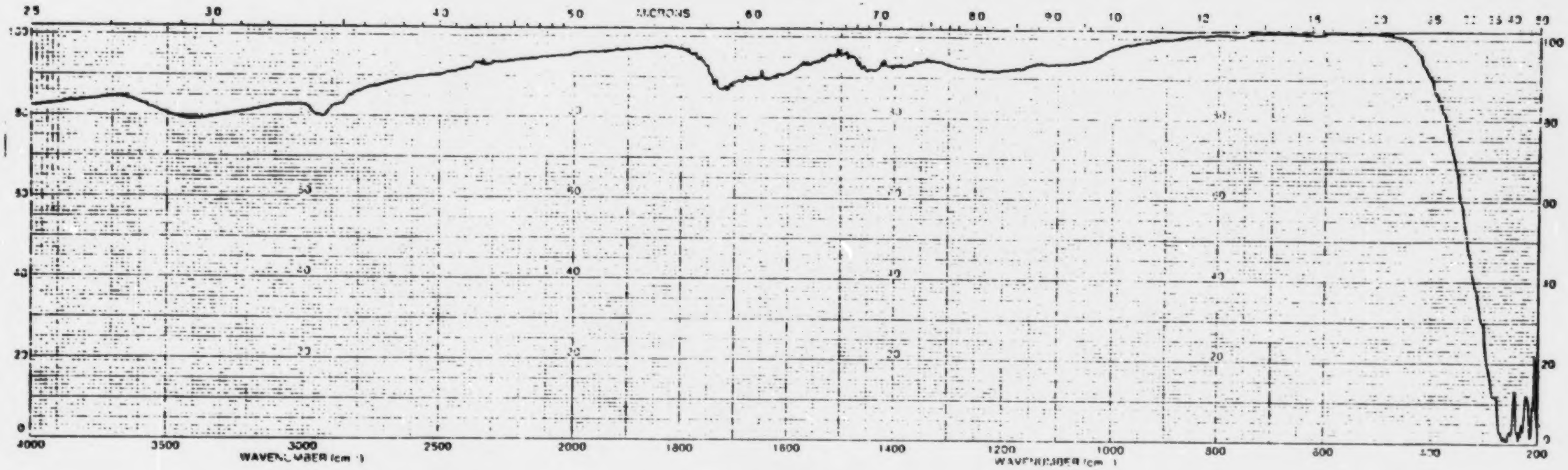

Figure B-30 Infrared Spectrum of the Meota Neutral Fraction (N_2) From Chromatography.

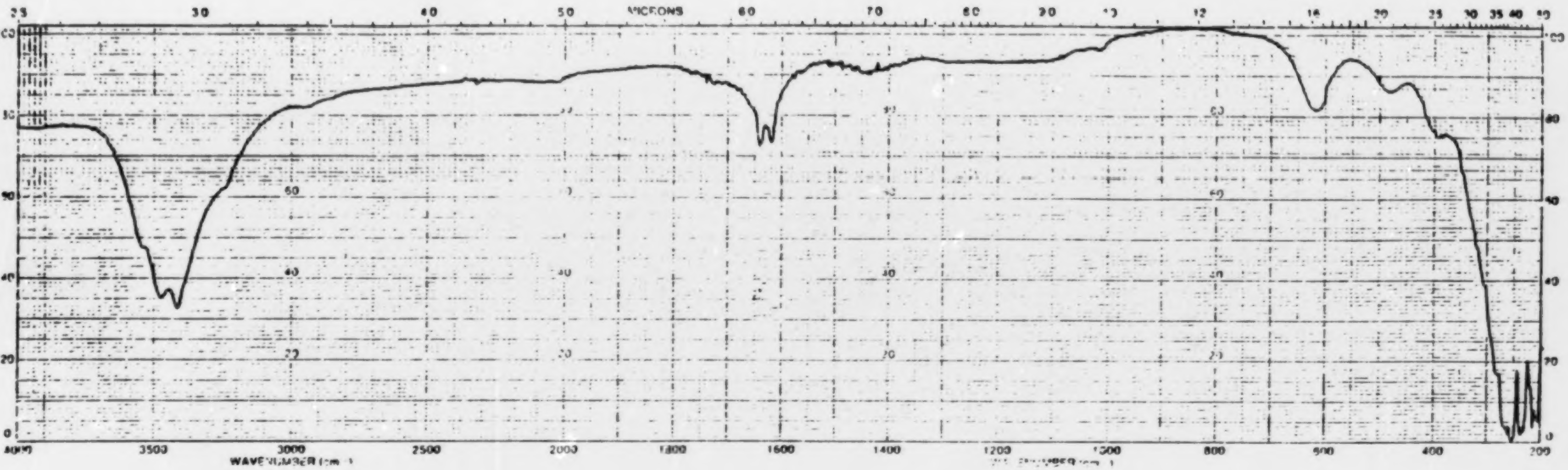

Figure B-31 Infrared Spectrum of the Battrum Basic Fraction (B_1) From Chromatography.

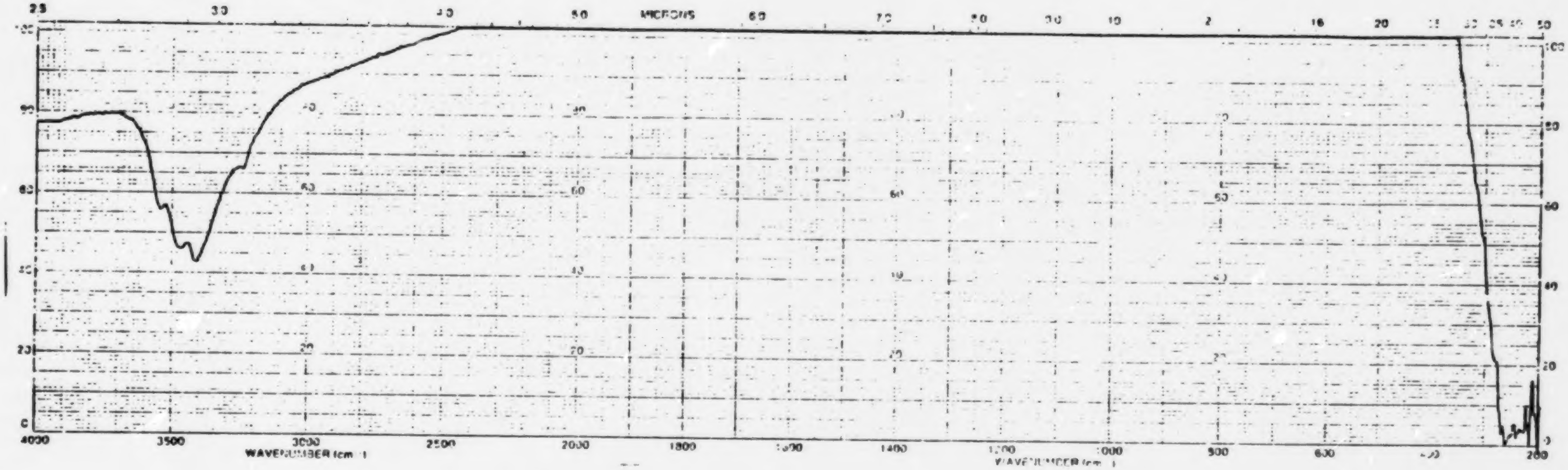

Figure B-32 Infrared Spectrum of the Eyehill Basic Fraction (B_1) From Chromatography.

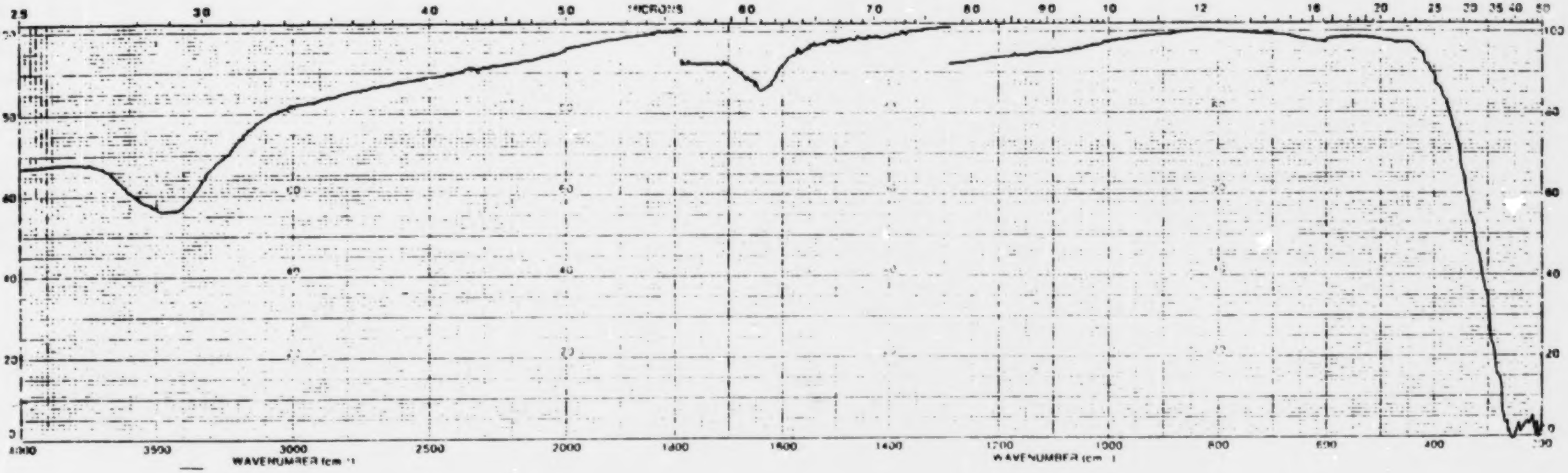

Figure B-33 Infrared Spectrum of the Eyehill Basic Fraction (B_1) From Chromatography.

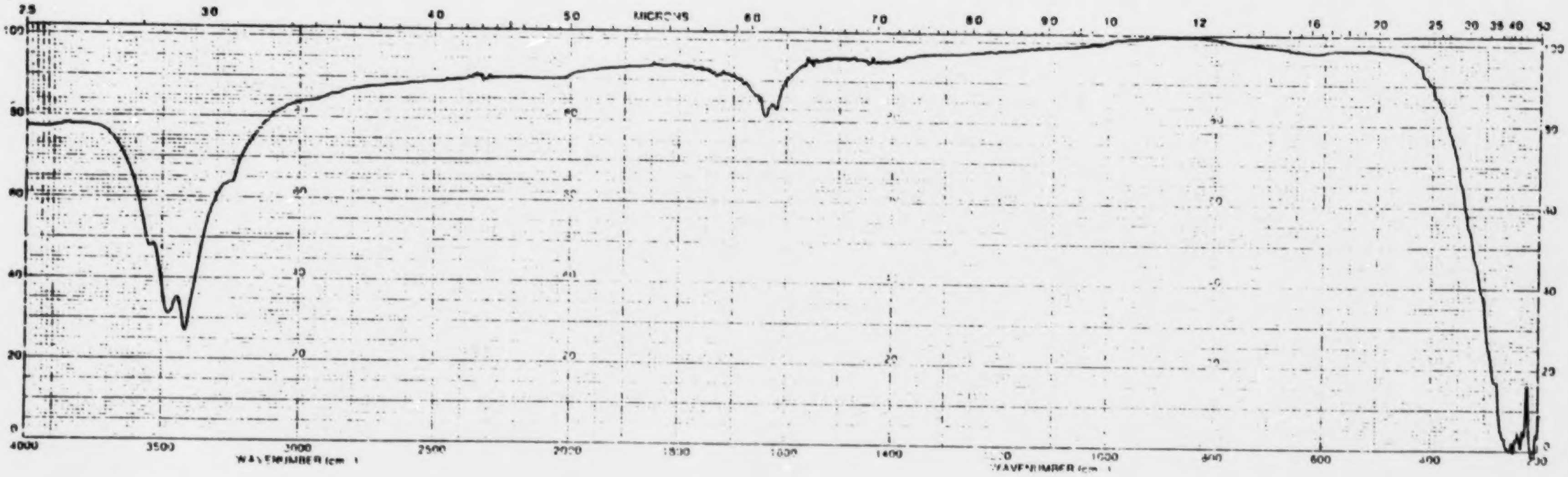

Figure B-34 Infrared Spectrum of the Fosterton Basic Fraction (B_1) From Chromatography.

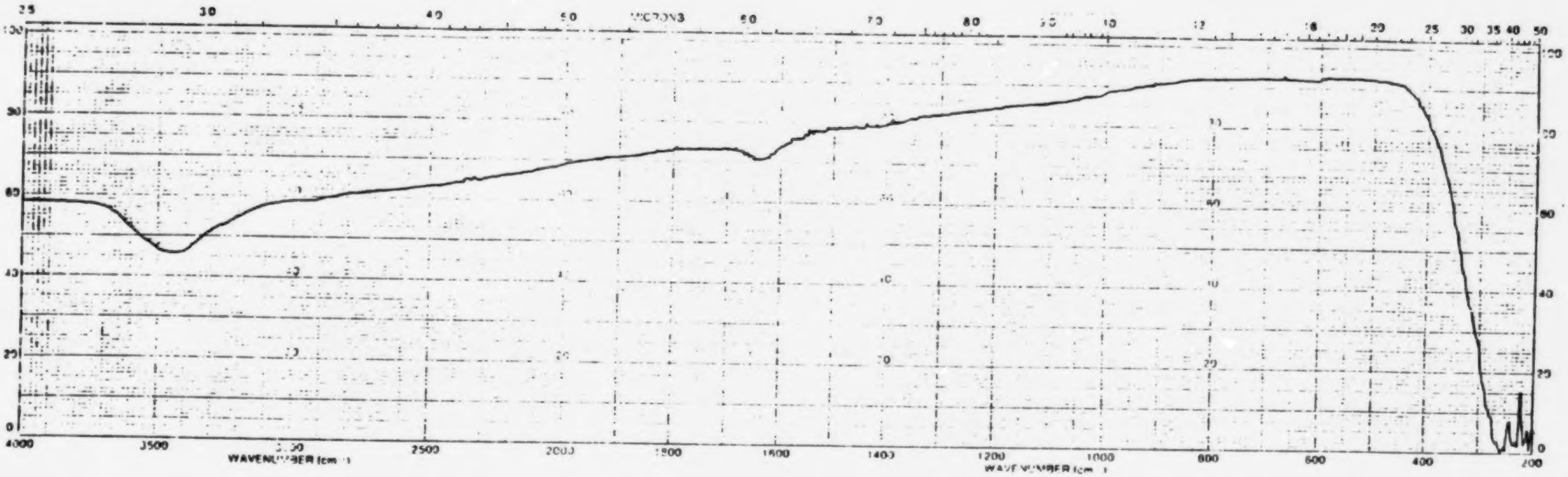

Figure B-35 Infrared Spectrum of the Lone Rock Basic Fraction (B_1) From Chromatography.

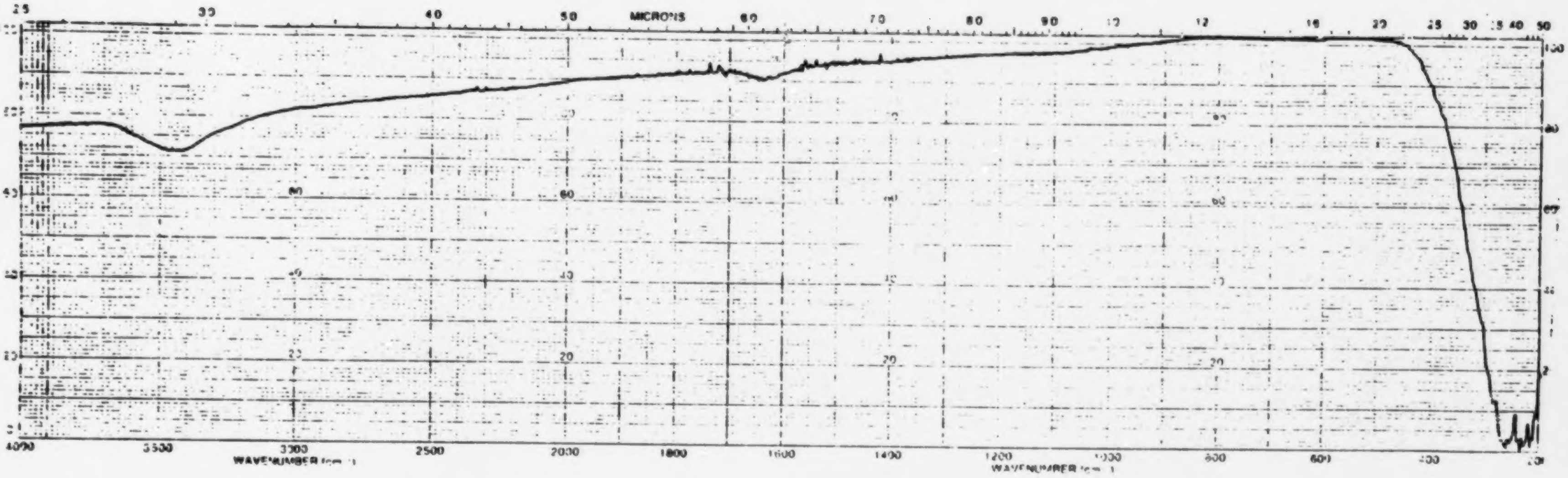

Figure B-36 Infrared Spectrum of the Meota Basic Fraction (B_1) From Chromatography.

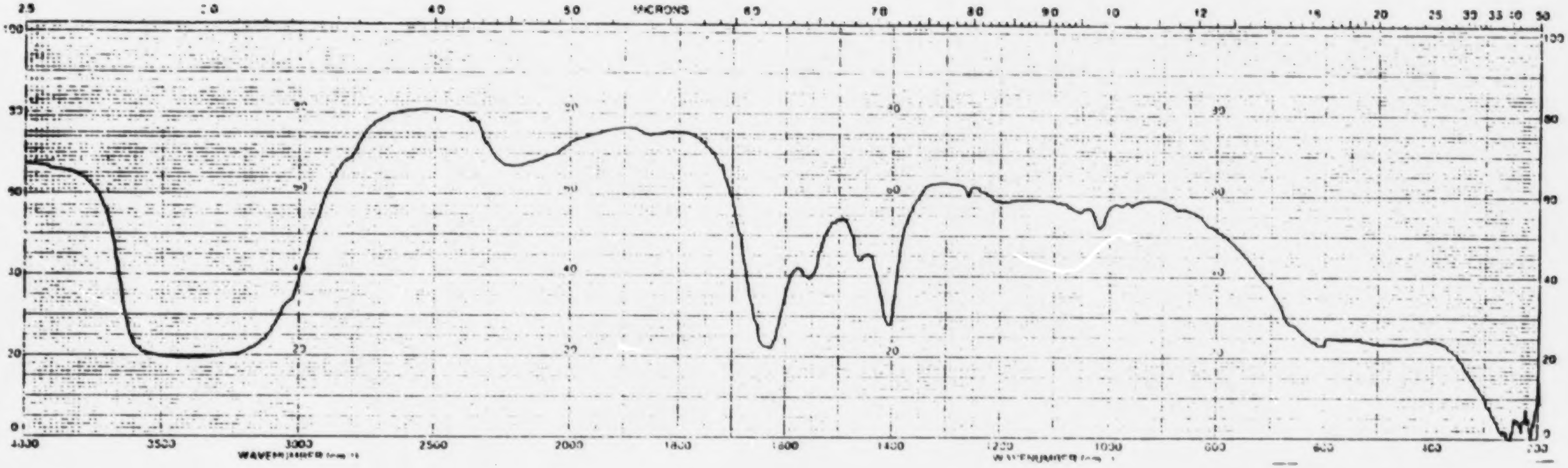

Figure B-37 Infrared Spectrum of the Battrum Basic Fraction (B_2) From Chromatography.

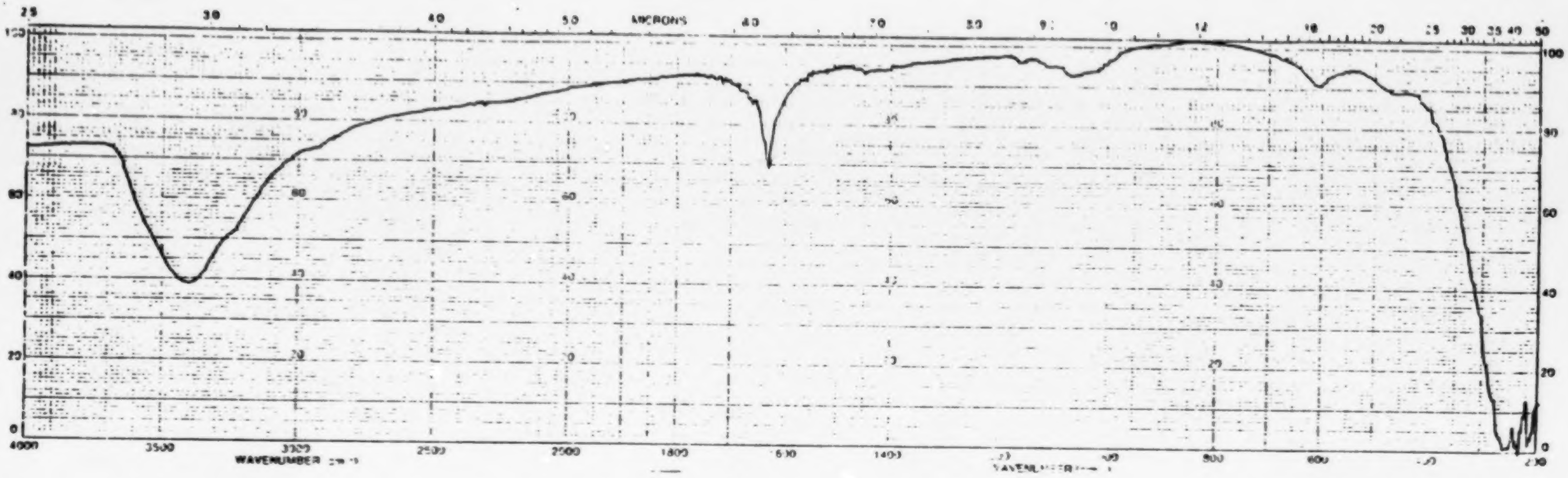

Figure B-38 Infrared Spectrum of the Eyehill Basic Fraction (B_2) From Chromatography.

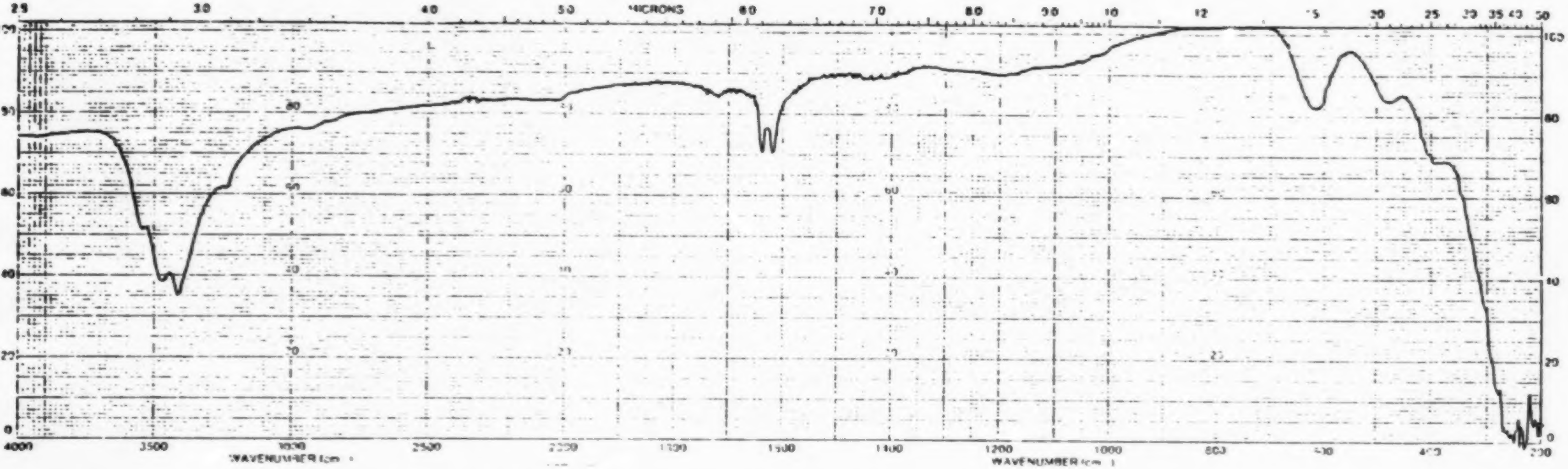

Figure B-39 Infrared Spectrum of the Fosterton Basic Fraction (B_2) From Chromatography.

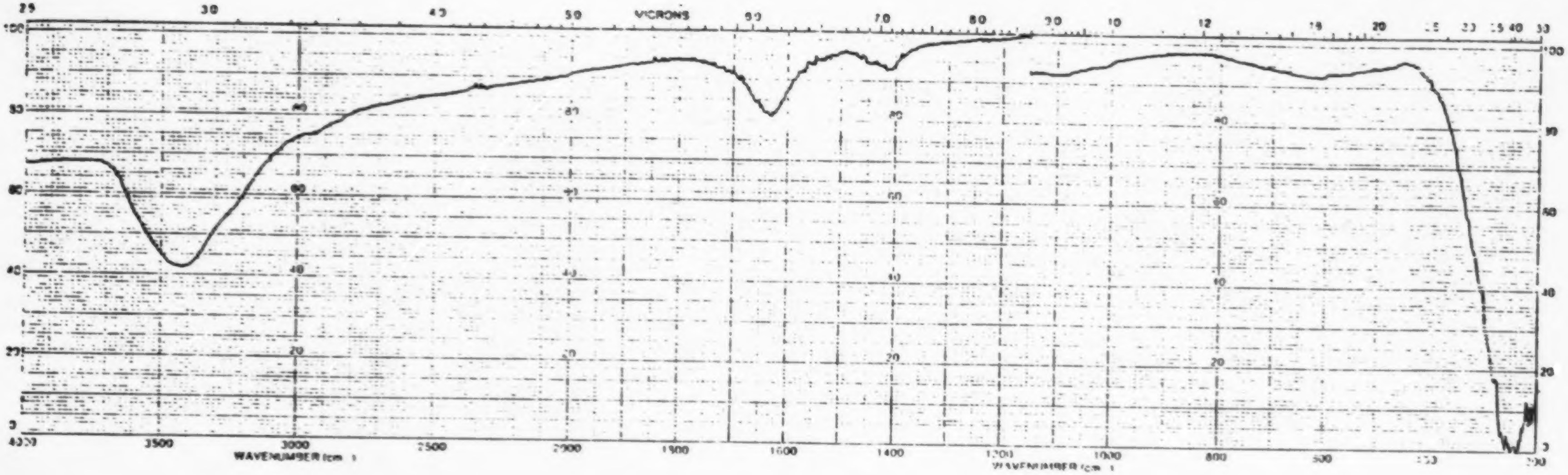

Figure B-40 Infrared Spectrum of the Meota Basic Fraction (B_2) From Chromatography.

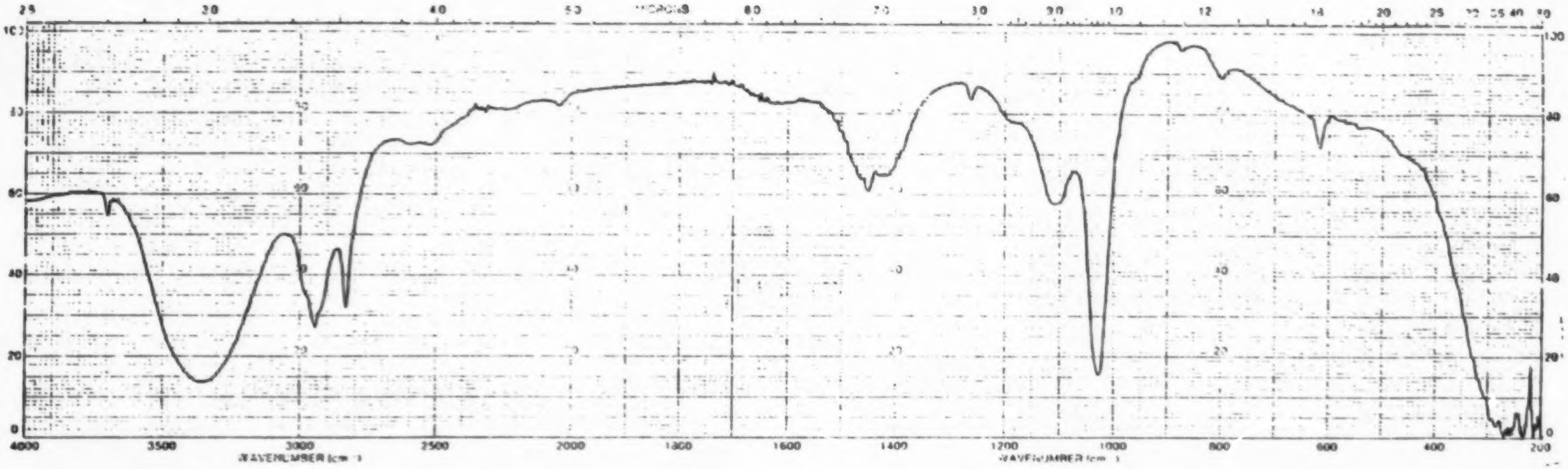

Figure B-41 Infrared Spectrum of Methanol